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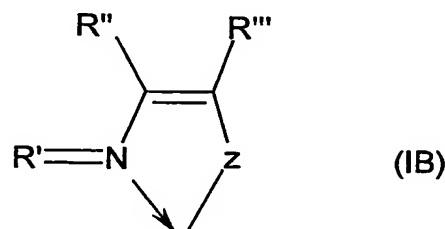
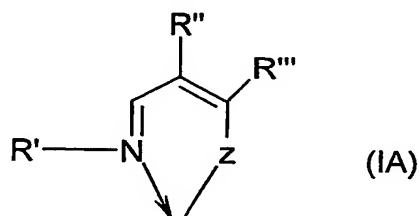
(43) International Publication Date
21 April 2005 (21.04.2005)

PCT

(10) International Publication Number
WO 2005/035121 A2

- (51) International Patent Classification⁷: **B01J 31/22**, 31/02, C07C 6/04
- (21) International Application Number:
PCT/BE2004/000146
- (22) International Filing Date: 15 October 2004 (15.10.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
03447257.1 16 October 2003 (16.10.2003) EP
60/529,010 12 December 2003 (12.12.2003) US
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- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Declaration under Rule 4.17:**
— of inventorship (Rule 4.17(iv)) for US only
- Published:**
— without international search report and to be republished upon receipt of that report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: **SCHIFF BASE METAL COMPLEXES FOR USE AS CATALYSTS IN ORGANIC SYNTHESIS**



(57) Abstract: This invention relates to metal complexes which are useful as catalysts components in olefin metathesis reactions, atom or group transfer radical polymerisation or addition reactions and vinylation reactions.

SCHIFF BASE METAL COMPLEXES FOR USE AS CATALYSTS IN ORGANIC SYNTHESIS.

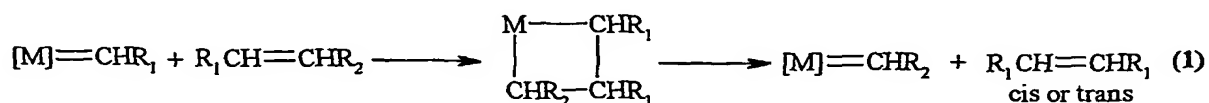
The present invention relates to transition metal complexes which are useful as catalyst components, either alone or in combination with co-catalysts or initiators, in a wide variety of organic synthesis reactions including olefin metathesis, acetylene metathesis and reactions involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate, such as atom transfer radical polymerisation, atom transfer radical addition, vinylation, cyclopropanation of ethylenically unsaturated compounds, epoxidation, oxidative cyclisation, aziridination, cyclopropanation of alkynes, Diels-Alder reactions, Michael addition, aldol condensation of ketones or aldehydes, Robinson annulation, hydroboration, hydrosilylation, hydrocyanation of olefins and alkynes, allylic alkylation, Grignard cross-coupling, oxidation of organic compounds (including saturated hydrocarbons, sulfides, selenides, phosphines and aldehydes), hydroamidation, isomerization of alcohols into aldehydes, aminolysis of olefins, hydroxylation of olefins, hydride reduction, Heck reactions, and hydrogenation of olefins or ketones.

The present invention also relates to methods for making said transition metal complexes and to novel intermediates involved in such methods.

The present invention also relates to obtaining polymers with extremely narrow molecular weight distribution by means of a living polymerisation reaction. The present invention further relates to certain derivatives of the said metal complexes which are suitable for covalent bonding to a carrier, the product of such covalent bonding being useful as a supported catalyst for heterogeneous catalytic reactions. More particularly, the present invention relates to certain Schiff base complexes of metals such as ruthenium and their use as catalysts for ring-opening metathesis polymerisation of cyclic olefins, atom transfer radical polymerisation of styrenes or (meth)acrylic esters, and for quinoline synthesis.

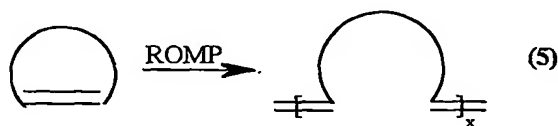
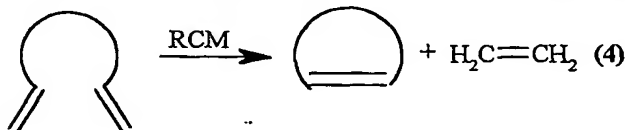
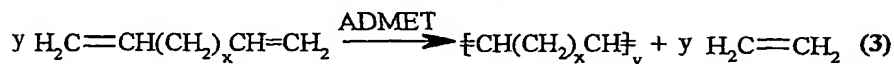
BACKGROUND OF THE INVENTION

Olefin metathesis is a catalytic process including, as a key step, a reaction between a first olefin and a first transition metal alkylidene complex, thus producing an unstable intermediate metallacyclobutane ring which then undergoes transformation into a second olefin and a second transition metal alkylidene complex according to equation (1) hereunder. Reactions of this kind are reversible and in competition with one another, so the overall result heavily depends on their respective rates and, when formation of volatile or insoluble products occur, displacement of equilibrium.



Several exemplary but non-limiting types of metathesis reactions for mono-olefins or diolefins are shown in equations (2) to (5) herein-after. Removal of a product, such as ethylene in equation (2), from the system can dramatically alter the course and/or rate of a desired metathesis

reaction, since ethylene reacts with an alkylidene complex in order to form a methylene ($M=CH_2$) complex, which is the most reactive and also the least stable of the alkylidene complexes.



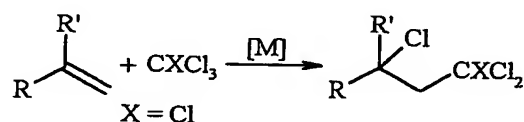
Of potentially greater interest than homo-coupling (equation 2) is cross-coupling between two different terminal olefins. Coupling reactions involving dienes lead to linear and cyclic dimers, oligomers, and, ultimately, linear or cyclic polymers (equation 3). In general, the latter reaction called acyclic diene metathesis (hereinafter referred to as ADMET) is favoured in highly concentrated solutions or in bulk, while cyclisation is favoured at low concentrations. When intramolecular coupling of a diene occurs so as to produce a cyclic alkene, the process is called ring-closing metathesis (hereinafter referred to as RCM) (equation 4). Strained cyclic olefins can be opened and oligomerised or polymerised (ring opening metathesis polymerisation, hereinafter referred to as ROMP, shown in equation 5). When the alkylidene catalyst reacts more rapidly with the cyclic olefin (e.g. a norbornene or a cyclobutene) than with a carbon-carbon double bond in the growing polymer chain, then a "living ring opening metathesis polymerisation" may result, i.e. there is little termination during or after the polymerization reaction.

A large number of catalyst systems comprising well-defined single component metal carbene complexes have been prepared and utilized in olefin metathesis. One major development in olefin metathesis was the discovery of the ruthenium and osmium carbene complexes by Grubbs and co-workers. U.S. Patent No. 5,977,393 discloses Schiff base derivatives of such compounds, which are useful as olefin metathesis catalysts, wherein the metal is coordinated by a neutral electron donor, such as a triarylphosphine or a tri(cyclo)alkylphosphine, and by an anionic ligand. Such catalysts show an improved thermal stability while maintaining metathesis activity even in polar protic solvents. They are also able to cyclise diallylamine hydrochloride to dihydropyrrole hydrochloride. Remaining problems to be solved with the carbene complexes of Grubbs are (i) improving both catalyst stability (i.e. slowing down decomposition) and metathesis activity at the same time and (ii) broadening the range of organic products achievable by using such catalysts, e.g. providing ability to ring-close highly substituted dienes into tri- and tetra-substituted olefins.

On the other hand, living polymerisation systems were reported for anionic and cationic polymerisation, however their industrial application has been limited by the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions. In contrast, free-radical polymerisation is the most popular commercial process to yield high molecular weight polymers. A

large variety of monomers can be polymerised and copolymerised radically under relatively simple experimental conditions which require the absence of oxygen but can be carried out in the presence of water. However free-radical polymerisation processes often yield polymers with ill-controlled molecular weights and high polydispersities. Combining the advantages of living polymerisation and radical polymerisation is therefore of great interest and was achieved by the atom (or group) transfer radical polymerisation process (hereinafter referred as ATRP) of U.S. Patent No. 5,763,548 involving (1) the atom or group transfer pathway and (2) a radical intermediate. This type of living polymerization, wherein chain breaking reactions such as transfer and termination are substantially absent, enables control of various parameters of the macromolecular structure such as molecular weight, molecular weight distribution and terminal functionalities. It also allows the preparation of various copolymers, including block and star copolymers. Living/controlled radical polymerization requires a low stationary concentration of radicals in equilibrium with various dormant species. It makes use of novel initiation systems based on the reversible formation of growing radicals in a redox reaction between various transition metal compounds and initiators such as alkyl halides, aralkyl halides or haloalkyl esters. ATRP is based on a dynamic equilibrium between the propagating radicals and the dormant species which is established through the reversible transition metal-catalysed cleavage of the covalent carbon-halogen bond in the dormant species. Polymerisation systems utilising this concept have been developed for instance with complexes of copper, ruthenium, nickel, palladium, rhodium and iron in order to establish the required equilibrium.

Due to the development of ATRP, further interest appeared recently for the Kharasch addition reaction, consisting in the addition of a polyhalogenated alkane across an olefin through a radical mechanism (first published by Kharasch et al. in *Science* (1945) 102:169) according to the following scheme (wherein X may be hydrogen or chloro or bromo, and R and R' may be each independently selected from hydrogen, C₁₋₇ alkyl, phenyl and carboxylic acid or ester):



Because ATRP is quite similar to the Kharasch addition reaction, the latter may also be called Atom Transfer Radical Addition (hereinafter referred as ATRA) and attracted interest in transition metal catalysis. Research in this field also focused on the use of new olefins and telogens and a wide range of internal, terminal and cyclic olefins and diolefins were tested with a wide range of polyhalides including fluoro, chloro, bromo and iodo as halogen atoms, as described for instance in *Eur. Polym. J.* (1980) 16:821 and *Tetrahedron* (1972) 28:29.

International patent application published as WO 03/062253 discloses five-coordinate metal complexes, salt, solvates or enantiomers thereof, comprising a carbene ligand, a multidentate ligand and one or more other ligands, wherein at least one of said other ligands is a constraint steric hindrance ligand having a pKa of at least 15. More specifically, the said document discloses

five-coordinate metal complexes having one of the general formulae (IA) and (IB) referred to in figure 3 thereof, wherein:

- M is a metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, preferably a metal selected from ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel and cobalt;
 - Z is selected from the group consisting of oxygen, sulphur, selenium, NR^{'''}, PR^{'''}, AsR^{'''} and SbR^{'''};
 - R^{''}, R^{'''} and R^{'''} are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, aryl and heteroaryl, or R^{''} and R^{'''} together form an aryl or heteroaryl radical, each said radical (when different from hydrogen) being optionally substituted with one or more, preferably 1 to 3, substituents R₅ each independently selected from the group consisting of halogen atoms, C₁₋₆ alkyl, C₁₋₆ alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, C₁₋₆ alkyl-C₁₋₆ alkoxysilyl, C₁₋₆ alkyl-aryloxysilyl, C₁₋₆ alkyl-C₃₋₁₀ cycloalkoxysilyl, alkylammonium and arylammonium;
 - R' is either as defined for R^{''}, R^{'''} and R^{'''} when included in a compound having the general formula (IA) or, when included in a compound having the general formula (IB), is selected from the group consisting of C₁₋₆ alkylene and C₃₋₈ cycloalkylene, the said alkylene or cycloalkylene group being optionally substituted with one or more substituents R₅;
 - R₁ is a constraint steric hindrance group having a pKa of at least about 15;
 - R₂ is an anionic ligand;
 - R₃ and R₄ are each hydrogen or a radical selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryl, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium and arylammonium;
 - R' and one of R₃ and R₄ may be bonded to each other to form a bidentate ligand;
 - R^{'''} and R^{'''} may be bonded to each other to form an aliphatic ring system including a heteroatom selected from the group consisting of nitrogen, phosphorous, arsenic and antimony;
 - R₃ and R₄ together may form a fused aromatic ring system, and
 - y represents the number of sp₂ carbon atoms between M and the carbon atom bearing R₃ and R₄ and is an integer from 0 to 3 inclusive,
- salts, solvates and enantiomers thereof.

These five-coordinate metal complexes including a carbene ligand proved to be very efficient olefin metathesis catalysts but also very efficient components in the catalysis or initiation of atom (or group)-transfer radical reactions such as ATRP or ATRA, as well as vinylation reactions, e.g. enol-ester synthesis. The same document also discloses that the Schiff base derivatives of ruthenium and osmium of U.S. Patent No. 5,977,393 as well as the corresponding derivatives of other

transition metals, may also be used in the catalysis or initiation of atom (or group) transfer radical reactions such as ATRP or ATRA, as well as vinylation reactions, e.g. enol-ester synthesis.

However there is a continuous need in the art for improving catalyst efficiency, i.e. improving the yield of the reaction catalysed by the said catalyst component after a certain period of time under given conditions (e.g. temperature, pressure, solvent and reactant/catalyst ratio) or else, at a given reaction yield, providing milder conditions (lower temperature, pressure closer to atmospheric pressure, easier separation and purification of product from the reaction mixture) or requiring a smaller amount of catalyst (i.e. a higher reactant/catalyst ratio) and thus resulting in more economic and environment-friendly operating conditions. This need is still more stringent for use in reaction-injection molding (RIM) processes such as, but not limited to, the bulk polymerisation of endo- or exo-dicyclopentadiene, or formulations thereof.

WO 93/20111 describes osmium- and ruthenium-carbene compounds with phosphine ligands as purely thermal catalysts for ring-opening metathesis polymerization of strained cycloolefins, in which cycloolefins such as dicyclopentadiene act as catalyst inhibitors and cannot be polymerized. This is confirmed for instance by example 3 of U.S. Patent No. 6,284,852, wherein dicyclopentadiene did not yield any polymer, even after days in the presence of certain ruthenium carbene complexes having phosphine ligands. However, U. S. Patent No. 6,235,856 teaches that dicyclopentadiene is accessible to thermal metathesis polymerization with a single-component catalyst if carbene-free ruthenium(II)- or osmium(II)-phosphine catalysts are used.

Experiments have shown that the efficiency of ruthenium alkylidene complexes in olefin metathesis reactions is inversely proportional to their activity in ATRP and ATRA, i.e. the most efficient catalysts for olefin metathesis reactions display the lowest activity in ATRP and ATRA. Therefore, there is a need in the art for a catalyst component which is able to display a high efficiency both in olefin metathesis reactions and in ATRP and ATRA. There is also a need in the art for a catalyst component which is able to initiate olefin metathesis reactions under very mild conditions, e.g. at room temperature. Finally there is also a need in the art for a catalyst component which is able to initiate vinylation reactions with high efficiency.

Furthermore, since presently available synthetic routes to the catalysts of U.S. Patent No. 5,977,393 proceed through the transformation of a ruthenium bisphosphane carbene, the development of catalysts with equivalent or better performance characteristics but synthesised directly from less expensive and more readily available starting materials, including from other transition metals, still corresponds to a need in the art.

All the above needs constitute the various goals to be achieved by the present invention.

SUMMARY OF THE INVENTION

The present invention is based on a first unexpected finding that efficient olefin metathesis catalysts can be obtained from metal complexes, in particular ruthenium complexes, which do not include an alkylidene ligand. Other unexpected findings of the invention are that efficient olefin metathesis catalysts can also be obtained by coordinating a metal such as ruthenium with:

- specifically substituted tetradentate ligands comprising two Schiff bases linked through a linking group having strongly electron-withdrawing substituents, or
- a combination of two anionic ligands, a non-anionic unsaturated ligand and an aliphatic saturated monoamine.

5 Another finding of the present invention is that such novel metal complexes as well as some known metal complexes, either used as such or supported onto a carrier, are efficient catalysts in organic synthesis reactions such as acetylene metathesis and reactions involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate, such as atom transfer radical polymerisation or addition, vinylation, cyclopropanation of
10 ethylenically unsaturated compounds, quinoline synthesis, epoxidation, oxidation of organic compounds (including saturated hydrocarbons, sulfides, selenides, phosphines and aldehydes), cyclopropanation of alkynes, hydrocyanation of olefins and alkynes, hydrosilylation of olefins or alkynes or ketones, aziridination of olefins, hydroamidation, hydrogenation of olefins or ketones, aminolysis of olefins, isomerisation of alcohols into aldehydes, Grignard cross-coupling,
15 hydroboration, Michael addition, aldol condensation of ketones or aldehydes, Robinson annulation, codimerisation of alkenes, hydroxylation of olefins, hydride reduction, allylic alkylation, Heck reactions, and Diels-Alder reactions.

BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 schematically shows the general formulae (IA) and (IB) of bidentate Schiff base ligands that are suitable for coordination in metal complexes according to an embodiment of the present invention.

Figure 2 schematically shows the general formulae (IIA), (IIB) and (IIC) of tetradentate ligands having two Schiff bases that are suitable for coordination in metal complexes according to
25 another embodiment of the present invention.

Figure 3 schematically shows the general formulae (IIIA) and (IIIB) of tetradentate Schiff base ligands and the general formula (IIIC) of bidentate ligands that are suitable for coordination in metal complexes according to another embodiment of the present invention.

30 Figure 4 shows the proton nuclear magnetic resonance spectrum of a Schiff base ligand that is suitable for coordination in the metal complexes according to an embodiment of the present invention.

Figure 5 schematically shows the general formula (IV) of tridentate Schiff base ligands that are suitable for coordination in metal complexes according to another embodiment of the present invention.

35 Figure 6 schematically shows general formulae (V) and (VI) of pyrrolaldimine ligands that are suitable for coordination in metal complexes according to another embodiment of the present invention.

DEFINITIONS

As used herein, the term complex, or coordination compound, refers to the result of a donor-acceptor mechanism or Lewis acid-base reaction between a metal (the acceptor) and several neutral molecules or ionic compounds called ligands, each containing a non-metallic atom or ion (the donor). Ligands that have more than one atom with lone pairs of electrons (i.e. more than one point of attachment to the metal center) and therefore occupy more than one coordination site are called multidentate ligands. The latter, depending upon the number of coordination sites occupied, include bidentate, tridentate and tetradentate ligands.

As used herein, the term " monometallic " refers to a complex in which there is a single metal center.

As used herein, the term " heterobimetallic " refers to a complex in which there are two different metal centers.

As used herein, the term " homobimetallic " refers to a complex having two identical metal centers, which however need not have identical ligands or coordination number.

As used herein, the term " metal " refers to a transition metal belonging to any of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table such as, but not limited to, iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

As used herein with respect to a substituting radical, ligand or group, the term " C₁₋₇ alkyl " means straight and branched chain saturated acyclic hydrocarbon monovalent radicals having from 1 to 7 carbon atoms such as, for example, methyl, ethyl, propyl, n-butyl, 1-methylethyl (isopropyl), 2-methylpropyl (isobutyl), 1,1-dimethylethyl (ter-butyl), 2-methylbutyl, n-pentyl, dimethylpropyl, n-hexyl, 2-methylpentyl, 3-methylpentyl, n-heptyl and the like; optionally the carbon chain length of such group may be extended to 20 carbon atoms.

As used herein with respect to a substituting radical, and unless otherwise stated, the term " acyl " broadly refers to a carbonyl (oxo) group adjacent to a C₁₋₇ alkyl radical, a C₃₋₁₀ cycloalkyl radical, an aryl radical, an arylalkyl radical or a heterocyclic radical, all of them being such as herein defined; representative examples include acetyl, benzoyl, naphthoyl and the like; similarly, the term " thioacyl " refers to a C=S (thioxo) group adjacent to one of said radicals.

As used herein with respect to a linking group, the term " C₁₋₇ alkylene " means the divalent hydrocarbon radical corresponding to the above defined C₁₋₇ alkyl, such as methylene, bis(methylene), tris(methylene), tetramethylene, hexamethylene and the like.

As used herein with respect to a substituting radical, ligand or group, the term " C₃₋₁₀ cycloalkyl " mean a mono- or polycyclic saturated hydrocarbon monovalent radical having from 3 to 10 carbon atoms, such as for instance cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl and the like, or a C₇₋₁₀ polycyclic saturated hydrocarbon monovalent radical having from 7 to 10 carbon atoms such as, for instance, norbornyl, fenchyl, trimethyltricycloheptyl or adamantyl.

As used herein with respect to a substituting radical, and unless otherwise stated, the term " C₃₋₁₀ cycloalkyl-alkyl " refers to an aliphatic saturated hydrocarbon monovalent radical (preferably

a C₁₋₇ alkyl such as defined above) to which a C₃₋₁₀ cycloalkyl (such as defined above) is already linked such as, but not limited to, cyclohexylmethyl, cyclopentylmethyl and the like.

As used herein with respect to a linking group, and unless otherwise stated, the term " C₃₋₁₀ cycloalkylene" means the divalent hydrocarbon radical corresponding to the above defined C₃₋₁₀ cycloalkyl, such as 1,2-cyclohexylene and 1,4-cyclohexylene.

As used herein with respect to a substituting radical, ligand or group, and unless otherwise stated, the term " aryl " designates any mono- or polycyclic aromatic monovalent hydrocarbon radical having from 6 up to 30 carbon atoms such as but not limited to phenyl, naphthyl, anthracenyl, phenanthracenyl, fluoranthenyl, chrysenyl, pyrenyl, biphenyl, terphenyl, picenyl, indenyl, biphenyl, indacenyl, benzocyclobutenyl, benzocyclooctenyl and the like, including fused benzo-C₄₋₈ cycloalkyl radicals (the latter being as defined above) such as, for instance, indanyl, tetrahydronaphthyl, fluorenyl and the like, all of the said radicals being optionally substituted with one or more substituents selected from the group consisting of halogen, amino, hydroxyl, sulfhydryl and nitro, such as for instance 4-fluorophenyl, 4-chlorophenyl, 3,4-dichlorophenyl, 2,6-diisopropyl-4-bromophenyl, pentafluorophenyl, 4-cyanophenyl, 2,6-dichlorophenyl, 2-fluorophenyl, 3-chlorophenyl, 3,5-dichlorophenyl and the like.

As used herein with respect to a linking group, and unless otherwise stated, the term "arylene" means the divalent hydrocarbon radical corresponding to the above defined aryl, such as phenylene, naphthylene and the like.

As used herein with respect to a combination of two substituting hydrocarbon radicals, and unless otherwise stated, the term " homocyclic" means a mono- or polycyclic, saturated or mono-unsaturated or polyunsaturated hydrocarbon radical having from 4 up to 15 carbon atoms but including no heteroatom in the said ring; for instance the said combination forms a C₂₋₆ alkylene radical, such as tetramethylene, which cyclizes with the carbon atoms to which the said two substituting hydrocarbon radicals are attached.

As used herein with respect to a substituting radical (including the combination of two substituting radicals), ligand or group, and unless otherwise stated, the term " heterocyclic " means a mono- or polycyclic, saturated or mono-unsaturated or polyunsaturated monovalent hydrocarbon radical having from 2 up to 15 carbon atoms and including one or more heteroatoms in one or more heterocyclic rings, each of said rings having from 3 to 10 atoms (and optionally further including one or more heteroatoms attached to one or more carbon atoms of said ring, for instance in the form of a carbonyl or thiocarbonyl or selenocarbonyl group, and/or to one or more heteroatoms of said ring, for instance in the form of a sulfone, sulfoxide, N-oxide, phosphate, phosphonate or selenium oxide group), each of said heteroatoms being independently selected from the group consisting of nitrogen, oxygen, sulfur, selenium and phosphorus, also including radicals wherein a heterocyclic ring is fused to one or more aromatic hydrocarbon rings for instance in the form of benzo-fused, dibenzo-fused and naphtho-fused heterocyclic radicals; within this definition are included heterocyclic radicals such as, but not limited to, diazepinyl, oxadiazinyl, thiadiazinyl, dithiazinyl, triazolonyl, diazepinonyl, triazepinyl, triazepinonyl, tetrazepinonyl, benzoquinolinyl, benzothiazinyl, benzothiazinonyl, benzoxathiinyl, benzodioxinyl, benzodithiinyl, benzoxazepinyl,

benzo-thiazepinyl, benzodiazepinyl, benzodioxepinyl, benzodithiepinyl, benzoxazocinyl, benzothiazocinyl, benzodiazocinyl, benzoxathiocinyl, benzo-dioxocinyl, benzotrioxepinyl, benzoxathiazepinyl, benzoxadiazepinyl, benzothiadiazepinyl, benzotriazepinyl, benzoxathiepinyl, benzotriazinonyl, benzoxazolinonyl, azetidinonyl, azaspirooundecyl, dithiaspirodecyl, selenazinyl, selenazolyl, selenophenyl, hypoxanthinyl, azahypoxanthinyl, bipyrazinyl, bipyridinyl, oxazolidinyl, diselenopyrimidinyl, benzodioxocinyl, benzopyrenyl, benzopyranonyl, benzophenazinyl, benzoquinoliziny, dibenzocarbazolyl, dibenzoacridinyl, dibenzophenazinyl, dibenzothiepinyl, dibenzooxepinyl, dibenzopyranonyl, dibenzoquinoxalinyl, dibenzothiazepinyl, dibenzoisoquinolinyl, tetraazaadamantyl, thiatetraazaadamantyl, oxauracil, oxazinyl, dibenzothiophenyl, dibenzofuranyl, oxazolinyl, oxazolonyl, azaindolyl, azolonyl, thiazolinyl, thiazolonyl, thiazolidinyl, thiazanyl, pyrimidonyl, thiopyrimidonyl, thiamorpholinyl, azlactonyl, naphthindazolyl, naphthindolyl, naphthothiazolyl, naphthothioxolyl, naphthoxindolyl, naphthotriazolyl, naphthopyranyl, oxabicycloheptyl, azabenzimidazolyl, azacycloheptyl, azacyclooctyl, azacyclononyl, azabicyclononyl, tetrahydrofuryl, tetrahydropyranyl, tetrahydropyryl, tetrahydroquinoleinyl, tetrahydrothienyl and dioxide thereof, dihydrothienyl dioxide, dioxindolyl, dioxinyl, dioxenyl, dioxazinyl, thioxanyl, thioxolyl, thiourazolyl, thiotriazolyl, thiopyranyl, thiopyryl, coumarinyl, quinoleinyl, oxyquinoleinyl, quinuclidinyl, xanthinyl, dihydropyranyl, benzodihydrofuryl, benzothiopyryl, benzothiopyranyl, benzoxazinyl, benzoxazolyl, benzodioxolyl, benzodioxanyl, benzothiadiaazolyl, benzotriazinyl, benzothiazolyl, benzoxazolyl, phenothioxinyl, phenothiazolyl, phenothieryl (benzothiopyranyl), phenopyryl, phenoxazolyl, pyridinyl, dihydropyridinyl, tetrahydropyridinyl, piperidinyl, morpholinyl, thiomorpholinyl, pyrazinyl, pyrimidinyl, pyridazinyl, triazinyl, tetrazinyl, triazolyl, benzotriazolyl, tetrazolyl, imidazolyl, pyrazolyl, thiazolyl, thiadiaazolyl, isothiazolyl, oxazolyl, oxadiaazolyl, pyrrolyl, furyl, dihydrofuryl, furoyl, hydantoinyl, dioxolanyl, dioxolyl, dithianyl, dithienyl, dithiyl, thienyl, indolyl, indazolyl, indolyl, indolizidinyl, benzofuryl, quinolyl, quinazolinyl, quinoxalinyl, carbazolyl, phenoxazinyl, phenothiazinyl, xanthenyl, purinyl, benzothieryl, naphthothieryl, thianthrenyl, pyranyl, pyryl, benzopyryl, isobenzofuranyl, chromenyl, phenoxathiyl, indoliziny, quinoliziny, isoquinolyl, phthalazinyl, naphthiridinyl, cinnoliny, pteridinyl, carboliny, acridinyl, perimidinyl, phenanthrolinyl, phenazinyl, phenothiazinyl, imidazoliny, imidazolidinyl, benzimidazolyl, pyrazolinyl, pyrazolidinyl, pyrrolinyl, pyrrolidinyl, piperazinyl, uridinyl, thymidinyl, cytidinyl, azirinyl, aziridinyl, diazirinyl, diaziridinyl, oxiranyl, oxaziridinyl, dioxiranyl, thiiranyl, azetyl, dihydroazetyl, azetidinyl, oxetyl, oxetanyl, oxetanonyl, homopiperazinyl, homopiperidinyl, thietyl, thietanyl, diazabicyclooctyl, diazetyl, diaziridinonyl, diaziridinethionyl, chromanyl, chromanonyl, thiochromanyl, thiochromanonyl, thiochromenyl, benzofuranyl, benzisothiazolyl, benzocarbazolyl, benzochromonyl, benzisoalloxazinyl, benzocoumarinyl, thiocoumarinyl, phenometoxazinyl, phenoparoxazinyl, phentriazinyl, thiodiazinyl, thiodiazolyl, indoxyl, thioindoxyl, benzodiazinyl (e.g. phthalazinyl), phthalidyl, phthalimidinyl, phthalazonyl, alloxazinyl, dibenzopyryl (i.e. xanthonyl), xanthionyl, isatyl, isopyrazolyl, isopyrazolonyl, urazolyl, urazinyl, uretanyl, uretidinyl, succinyl, succinimido, benzylsultimyl, benzylsultamyl and the like, including all possible isomeric forms thereof, wherein each carbon atom of said heterocyclic ring may be independently substituted with a substituent selected from the group consisting of halogen, nitro, C₁₋₇ alkyl (optionally containing

one or more functions or radicals selected from the group consisting of carbonyl (oxo), alcohol (hydroxyl), ether (alkoxy), acetal, amino, imino, oximino, alkyloximino, amino-acid, cyano, carboxylic acid ester or amide, nitro, thio C₁₋₇ alkyl, thio C₃₋₁₀ cycloalkyl, C₁₋₇ alkylamino, cycloalkylamino, alkenylamino, cycloalkenylamino, alkynylamino, arylamino, arylalkylamino, hydroxylalkylamino, mercaptoalkylamino, heterocyclic amino, heterocyclic-substituted alkylamino, heterocyclic-substituted arylamino, hydrazino, alkylhydrazino, phenylhydrazino, sulfonyl, sulfonamido and halogen), C₂₋₇ alkenyl, C₂₋₇ alkynyl, halo C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl, alkylacyl, arylacyl, hydroxyl, amino, C₁₋₇ alkylamino, cycloalkylamino, alkenylamino, cycloalkenylamino, alkynylamino, arylamino, arylalkylamino, hydroxyalkylamino, mercaptoalkylamino, heterocyclic amino, heterocyclic-substituted alkylamino, heterocyclic-substituted arylamino, hydrazino, alkylhydrazino, phenylhydrazino, sulfhydryl, C₁₋₇ alkoxy, C₃₋₁₀ cycloalkoxy, aryloxy, arylalkyloxy, oxyheterocyclic, heterocyclic-substituted alkyloxy, thio C₁₋₇ alkyl, thio C₃₋₁₀ cycloalkyl, thioaryl, thioheterocyclic, arylalkylthio, heterocyclic-substituted alkylthio, formyl, hydroxylamino, cyano, carboxylic acid or esters or thioesters or amides thereof, thiocarboxylic acid or esters or thioesters or amides thereof; depending upon the number of unsaturations in the 3 to 10 membered ring, heterocyclic radicals may be sub-divided into heteroaromatic (or "heteroaryl") radicals and non-aromatic heterocyclic radicals; when a heteroatom of the said non-aromatic heterocyclic radical is nitrogen, the latter may be substituted with a substituent selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl and alkylaryl.

As used herein with respect to a substituting radical, ligand or group, and unless otherwise stated, the terms "C₁₋₇ alkoxy", "C₂₋₇ alkenyloxy", "C₂₋₇ alkynyloxy", "C₃₋₁₀ cycloalkoxy", "aryloxy", "arylalkyloxy", "oxyheterocyclic", "thio C₁₋₇ alkyl", "thio C₃₋₁₀ cycloalkyl", "arylthio", "arylalkylthio" and "thioheterocyclic" refer to substituents wherein a C₁₋₇ alkyl, C₂₋₇ alkenyl or C₂₋₇ alkynyl (optionally the carbon chain length of such groups may be extended to 20 carbon atoms), respectively a C₃₋₁₀ cycloalkyl, aryl, arylalkyl or heterocyclic radical (each of them such as defined herein), are attached to an oxygen atom or a divalent sulfur atom through a single bond, such as but not limited to methoxy, ethoxy, propoxy, butoxy, pentoxy, isopropoxy, sec-butoxy, tert-butoxy, isopentoxy, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, thiomethyl, thioethyl, thiopropyl, thiobutyl, thiopentyl, thiocyclopropyl, thiocyclobutyl, thiocyclopentyl, thiophenyl, phenyloxy, benzyloxy, mercaptobenzyl, cresoxy and the like.

As used herein with respect to a substituting atom or ligand, the term halogen means any atom selected from the group consisting of fluorine, chlorine, bromine and iodine.

As used herein with respect to a substituting radical or group, and unless otherwise stated, the term "halo C₁₋₇ alkyl" means a C₁₋₇ alkyl radical (such as above defined, i.e. optionally the carbon chain length of such group may be extended to 20 carbon atoms) in which one or more hydrogen atoms are independently replaced by one or more halogens (preferably fluorine, chlorine or bromine), such as but not limited to difluoromethyl, trifluoromethyl, trifluoroethyl, octafluoropentyl, dodecafluoroheptyl, dichloromethyl and the like.

As used herein with respect to a substituting radical, ligand or group, and unless otherwise stated, the term "C₂₋₇ alkenyl" means a straight or branched acyclic hydrocarbon monovalent

radical having one or more ethylenical unsaturations and having from 2 to 7 carbon atoms such as, for example, vinyl, 1-propenyl, 2-propenyl (allyl), 1-butenyl, 2-butenyl, 2-pentenyl, 3-pentenyl, 3-methyl-2-butenyl, 3-hexenyl, 2-hexenyl, 2-heptenyl, 1,3-butadienyl, pentadienyl, hexadienyl, heptadienyl, heptatrienyl and the like, including all possible isomers thereof; optionally the carbon chain length of such group may be extended to 20 carbon atoms.

As used herein with respect to a substituting radical, ligand or group, and unless otherwise stated, the term "C₃₋₁₀ cycloalkenyl" means a monocyclic mono- or polyunsaturated hydrocarbon monovalent radical having from 3 to 8 carbon atoms, such as for instance cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclopentadienyl, cyclohexenyl, cyclohexadienyl, cycloheptenyl, cycloheptadienyl, cycloheptatrienyl, cyclooctenyl, cyclooctadienyl, cyclooctatrienyl, 1,3,5,7-cyclooctatetraenyl and the like, or a C₇₋₁₀ polycyclic mono- or polyunsaturated hydrocarbon monovalent radical having from 7 to 10 carbon atoms such as dicyclopentadienyl, fenchenyl (including all isomers thereof, such as α -pinolenyl), bicyclo[2.2.1]hept-2-enyl (norbornenyl), bicyclo[2.2.1]hepta-2,5-dienyl (norbornadienyl), cyclofencheryl and the like.

As used herein with respect to a substituting radical, ligand or group, the term "C₂₋₇ alkynyl" defines straight and branched chain hydrocarbon radicals containing one or more triple bonds (i.e. acetylenic unsaturation) and optionally at least one double bond and having from 2 to 7 carbon atoms such as, for example, acetylenyl, 1-propynyl, 2-propynyl, 1-butylnyl, 2-butylnyl, 2-pentylnyl, 1-pentylnyl, 3-methyl-2-butylnyl, 3-hexynyl, 2-hexynyl, 1-penten-4-ynyl, 3-penten-1-ynyl, 1,3-hexadien-1-ynyl and the like, including all possible isomers thereof; optionally the carbon chain length of such group may be extended to 20 carbon atoms.

As used herein, and unless otherwise stated, the terms "arylalkyl", "arylalkenyl" and "heterocyclic-substituted alkyl" refer to an aliphatic saturated or ethylenically unsaturated hydrocarbon monovalent radical (preferably a C₁₋₇ alkyl or C₂₋₇ alkenyl radical such as defined above, i.e. optionally the carbon chain length of such group may be extended to 20 carbon atoms) onto which an aryl or heterocyclic radical (such as defined above) is already bonded, and wherein the said aliphatic radical and/or the said aryl or heterocyclic radical may be optionally substituted with one or more substituents independently selected from the group consisting of halogen, amino, hydroxyl, sulfhydryl, C₁₋₇ alkyl, trifluoromethyl and nitro, such as but not limited to benzyl, 4-chlorobenzyl, 4-fluorobenzyl, 2-fluorobenzyl, 3,4-dichlorobenzyl, 2,6-dichlorobenzyl, 3-methylbenzyl, 4-methylbenzyl, 4-*tert*-butylbenzyl, phenylpropyl, 1-naphthylmethyl, phenylethyl, 1-amino-2-phenylethyl, 1-amino-2-[4-hydroxyphenyl]ethyl, 1-amino-2-[indol-2-yl]ethyl, styryl, pyridylmethyl, pyridylethyl, 2-(2-pyridyl)isopropyl, oxazolylbutyl, 2-thienylmethyl, pyrrolylethyl, morpholinylethyl, imidazol-1-yl-ethyl, benzodioxolylmethyl and 2-furylmethyl.

As used herein, and unless otherwise stated, the terms "alkylcycloalkyl", "alkenyl (hetero)aryl", "alkyl(hetero)aryl", and "alkyl-substituted heterocyclic" refer respectively to an aryl, heteroaryl, cycloalkyl or heterocyclic radical (such as defined above) onto which are already bonded one or more aliphatic saturated or unsaturated hydrocarbon monovalent radicals, preferably one or more C₁₋₇ alkyl, C₂₋₇ alkenyl or C₃₋₁₀ cycloalkyl radicals as defined above, such as, but not limited to, o-toluylyl, m-toluylyl, p-toluylyl, 2,3-xylylyl, 2,4-xylylyl, 3,4-xylylyl, o-cumenylyl, m-cumenylyl, p-

cumenyl, o-cymenyl, m-cymenyl, p-cymenyl, mesityl, *ter*-butylphenyl, lutidinyl (i.e. dimethylpyridyl), 2-methylaziridinyl, methylbenzimidazolyl, methylbenzofuranyl, methylbenzothiazolyl, methylbenzotriazolyl, methylbenzoxazolyl, methylcyclohexyl and menthyl.

As used herein with respect to a substituting radical, and unless otherwise stated, the term "alkoxyaryl" refers to an aryl radical (such as defined above) onto which is (are) bonded one or more C₁₋₇ alkoxy radicals as defined above, preferably one or more methoxy radicals, such as, but not limited to, 2-methoxyphenyl, 3-methoxyphenyl, 4-methoxyphenyl, 3,4-dimethoxyphenyl, 2,4,6-trimethoxyphenyl, methoxynaphtyl and the like.

As used herein, and unless otherwise stated, the terms "alkylamino", "cycloalkylamino", "alkenylamino", "cycloalkenylamino", "arylamino", "arylalkylamino", "heterocyclic-substituted alkylamino", "heterocyclic-substituted arylamino", "heterocyclic amino", "hydroxyalkylamino", "mercaptoalkylamino" and "alkynylamino" mean that respectively one (thus monosubstituted amino) or even two (thus disubstituted amino) C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₂₋₇ alkenyl, C₃₋₁₀ cycloalkenyl, aryl, arylalkyl, heterocyclic-substituted alkyl, heterocyclic-substituted aryl, heterocyclic (provided in this case the nitrogen atom is attached to a carbon atom of the heterocyclic ring), mono- or polyhydroxy C₁₋₇ alkyl, mono- or polymercapto C₁₋₇ alkyl or C₂₋₇ alkynyl radical(s) (each of them as defined herein, respectively) is/are attached to a nitrogen atom through a single bond, such as but not limited to, anilino, benzylamino, methylamino, dimethylamino, ethylamino, diethylamino, isopropylamino, propenylamino, n-butylamino, *ter*-butylamino, dibutylamino, morpholinoalkylamino, 4-morpholinoanilino, hydroxymethylamino, β -hydroxyethylamino and ethynylamino; this definition also includes mixed disubstituted amino radicals wherein the nitrogen atom is attached to two such radicals belonging to two different sub-set of radicals, e.g. an alkyl radical and an alkenyl radical, or to two different radicals within the same sub-set of radicals, e.g. methylethylamino; among disubstituted amino radicals, symetrically substituted are usually preferred and more easily accessible.

As used herein, and unless otherwise stated, the terms "(thio)carboxylic acid (thio)ester" and "(thio)carboxylic-acid (thio)amide" refer to substituents wherein the carboxyl or thiocarboxyl group is bonded to the hydrocarbonyl residue of an alcohol, a thiol, a polyol, a phenol, a thiophenol, a primary or secondary amine, a polyamine, an amino-alcohol or ammonia, the said hydrocarbonyl residue being selected from the group consisting of C₁₋₇ alkyl, C₂₋₇ alkenyl, C₂₋₇ alkynyl, C₃₋₁₀ cycloalkyl, C₃₋₁₀ cycloalkenyl, aryl, arylalkyl, alkylaryl, alkylamino, cycloalkylamino, alkenylamino, cycloalkenylamino, arylamino, arylalkylamino, heterocyclic amino, heterocyclic-substituted alkylamino, heterocyclic-substituted arylamino, hydroxyalkylamino, mercapto-alkylamino or alkynylamino (each such as above defined, respectively).

As used herein with respect to a metal ligand, the terms alkylammonium and aryl-ammonium mean a tetra-coordinated nitrogen atom being linked to one or more C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl or heteroaryl groups, each such as above defined, respectively.

As used herein with respect to a metal ligand, and unless otherwise stated, the term "Schiff base" conventionally refers to the presence of an imino group (usually resulting from the reaction of a primary amine with an aldehyde or a ketone) in the said ligand, preferably being part of a

multidentate ligand (such as defined in <http://www.ilpi.com/organomet/coordnum.html>) which may be coordinated to the metal, in addition to the nitrogen atom of said imino group, through at least one further heteroatom selected from the group consisting of oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic and antimony. The said multidentate ligand may be for instance, but without limitation, selected from the group consisting of:

- a N,O-bidentate Schiff base ligand such as a lumazine or substituted lumazine or 2-(2-hydroxyphenyl)benzoxazole or (2'-hydroxyphenyl)-2-thiazoline;
- a N,S-bidentate Schiff base ligand such as a thiolumazine or substituted thiolumazine;
- a N,N-bidentate or N,O-bidentate or N,S-bidentate ligand being a salicylaldehyde such as the reaction product of an optionally substituted salicylaldehyde (such as, but not limited to, *tert*-butyl-salicylaldehyde, 6-phenyl-salicylaldehyde, 2-(9-phenanthrene) salicylaldehyde, 2-(9-anthracene) salicylaldehyde, 4-methoxysalicylaldehyde, 4-nitro-salicylaldehyde, 4,6-dichloro-salicylaldehyde, *p*-trifluoromethyl-salicylaldehyde, 3,5-dinitro-salicylaldehyde, 2-hydroxynaphthaldehyde, and nitration products thereof) with a primary amine, preferably an arylamine (more preferably an arylamine having one or more bulky substituents such as, but not limited to, 2,6-diisopropylaniline, 2,6-diisopropyl-4-nitroaniline, biphenylamine, terphenylamine, anthracenylamine, phenanthracenylamine, 2,6-dimethylphenyl, 2,6-diethylaniline, 4-methylaniline, 2-isopropyl-6-methylaniline, 2,4,6-trimethylaniline, 2-*tert*-butylaniline, 2-*tert*-butyl-6-methylaniline, and 10-nitroanthracenylamine) as shown in formula (VI) of figure 6 (wherein A is selected from the group consisting of oxygen, sulfur and nitrogen; R is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl, provided that R represents at least one hydrogen atom and z is 1 when A is oxygen or sulfur or z is 2 when A is nitrogen; R¹ is selected from the group consisting of C₁₋₇ alkyl, aryl, arylalkyl, siloxyl, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl; R² is selected from the group consisting of hydrogen, C₁₋₇ alkyl, aryl and halogen; R³ is hydrogen; R⁴ is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl; and R⁵ is selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl), a representative example of these ligands being 2,3-dihydroxy-1-(2,6-diisopropyl)benzaldehyde;
- a N,N-bidentate ligand such as a bis(oxazoline), a 2,2'-bipyridine, a 2,2'-bipyridyliminato, a 2,2'-biimidazole, a 1,10-phenanthroline, a 1,4-benzoquinonediimine, a N,N'-di(C₃₋₁₀ cycloalkyl)-1,4-diazabutadiene (in particular N,N'-dicyclohexyl-1,4-diazabutadiene and N,N'-diadamantyl-1,4-diazabutadiene), a N,N'-diaryl-1,4-diazabutadiene (in particular N,N'-dimesityl-1,4-diazabutadiene, N,N'-dixyl-1,4-diazabutadiene and N,N'-di[(2,6-diisopropyl)phenyl]-1,4-diazabutadiene), a Schiff base ligand such as may be obtained for instance through the condensation of 1,3-diaminopropane and pyrrole-2-carboxaldehyde, a pyrrolaldehyde such as the reaction product of an optionally substituted pyrrole-2-carboxaldehyde with a primary preferably aromatic amine (more preferably an arylamine having one or more bulky substituents such as, but not limited to, 2,6-diisopropylaniline, 2,6-diisopropyl-4-nitroaniline, biphenylamine, terphenylamine, anthracenylamine, phenanthracenylamine, 2,6-dimethylphenyl, 2,6-diethylaniline, 4-methylaniline, 2-isopropyl-6-methylaniline, 2,4,6-

trimethylaniline, 2-*tert*-butylaniline, 2-*tert*-butyl-6-methylaniline, and 10-nitroanthracenylamine) as shown in formula (V) of figure 6 (wherein R¹ is selected from the group consisting of C₁₋₇ alkyl, aryl, arylalkyl, siloxyl, nitro, sulfonate, halogen, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl; R² is selected from the group consisting of hydrogen, C₁₋₇ alkyl, aryl and halogen; R³ is hydrogen; R⁴ is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl; and R⁵ is selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl and aryl);

- a N,P-bidentate Schiff base ligand such as a phosphino-oxazoline;
- a N,Z-bidentate Schiff base ligand such as shown in figure 1, wherein Z is or includes an atom selected from the group consisting of oxygen, sulfur, selenium, nitrogen, phosphorus, arsenic and antimony; it may be advantageous for the said bidentate Schiff base ligand to further include a carbon-carbon double bond conjugated with the carbon-nitrogen double bond of the imino group, for instance as shown in figure 1;
- a N,N,O- tridentate Schiff base ligand such as derived from 6-amino-5-formyl-1,3-dimethyluracil and semicarbazide or acetylhydrazine or benzoylhydrazine, or such as derived from 7-formyl-8-hydroxyquinoline(oxine) and 2-aminophenol or 2-aminopyridine;
- a O,N,O-tridentate Schiff base ligand such as 6-amino-5-formyl-1,3-dimethyluracil-benzoyl-hydrazone, or such as the reaction product of a hydroxyaldehyde with an aminoalcohol shown in formula (IV) of figure 5 (wherein R₁ may be selected from the group consisting of hydrogen, halogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, C₁₋₇ alkoxy and arylalkyl; R₂ may be selected from the group consisting of hydrogen, halogen, nitro, C₁₋₇ alkyl, aryl and arylalkyl; R₃ may be hydrogen or aryl; R₄ may be selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl; and R₅ may be selected from the group consisting of hydrogen, aryl and alkylaryl), or *N*-(2-methoxyphenyl) salicylideneamine, or salicylaldehyde-2-hydroxanil, or the heterocyclic Schiff base resulting from the reaction of 1-amino-5-benzoyl-4-phenyl-1 H pyrimidin-2-one with 2-hydroxynaphtaldehyde, or the thenoyltrifluoroaceto antipyrine Schiff base resulting from the reaction of thenoyl-trifluoroacetone with 4-aminoantipyrine;
- a O,N,S-tridentate Schiff base ligand such as salicylaldehyde-2-mercaptoanil, *S*-benzyl-2-[(2-hydroxyphenyl)methylene]dithiocarbazate or 2-[(2-hydroxyphenyl)methylene]-*N*-phenylhydrazinecarbothioamide;
- a N,N,S-tridentate Schiff base ligand such as 6-amino-5-formyl-1,3-dimethyluracilthio-semicarbazone;
- a N,N,N-tridentate Schiff base ligand such as a pyridine bisoxazoline or 2-[(2-aminoethylimino)(phenyl)methyl]pyridine or tris(pyrazolyl)borate or as resulting from the reaction of 2-amino-1,3,4-thiadiazole with pyrrole-2-carboxaldehyde; and
- a N,N,P-tridentate Schiff base ligand such as a phosphino-2-oxazolinyquinoline.

By extension, the term " Schiff base " as used herein also refers to Schiff base ligands with thioether or coumarin groups. The multidentate ligand may include more than one Schiff base, for instance as shown in figures 2 and 3, thus possibly resulting in O,N,N,O-tetradentate or O,N,N,N-tetradentate or N,N,N,N-tetradentate Schiff base ligands.

As used herein, the terms " constraint steric hindrance " relates to a group or ligand, usually a branched or substituted group or ligand, which is constrained in its movements, i.e. a group the size of which produces a molecular distortion (either an angular distortion or a lengthening of bonds) being measurable by X-ray diffraction.

5 As used herein and unless otherwise stated, the term " stereoisomer " refers to all possible different isomeric as well as conformational forms which the compounds of the invention may possess, in particular all possible stereochemically and conformationally isomeric forms, all diastereomers, enantiomers and/or conformers of the basic molecular structure. Some compounds of the present invention may exist in different tautomeric forms, all of the latter being included
10 within the scope of the present invention.

As used herein and unless otherwise stated, the term " enantiomer " means each individual optically active form of a compound of the invention, having an optical purity or enantiomeric excess (as determined by methods standard in the art) of at least 80% (i.e. at least 90% of one enantiomer and at most 10% of the other enantiomer), preferably at least 90% and more preferably
15 at least 98%.

As used herein and unless otherwise stated, the term " solvate " includes any combination which may be formed by a compound of this invention with a suitable inorganic solvent (e.g. hydrates formed with water) or organic solvent, such as but not limited to alcohols (in particular ethanol and isopropanol), ketones (in particular methylethylketone and methylisobutylketone),
20 esters (in particular ethyl acetate) and the like.

DETAILED DESCRIPTION OF THE INVENTION

In a first aspect, the present invention relates to an at least tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- 25 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- 30 - a non-anionic unsaturated ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or with electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic
35 acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- a non-anionic ligand L² selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic
40 acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

In this first aspect of the invention, the multidentate ligand is preferably a multidentate Schiff base such as above defined, more preferably a N,O-bidentate Schiff base ligand or N,S-bidentate Schiff base ligand, most preferably a bidentate Schiff base ligand as shown in formulae (IA) or (IB) in figure 1 and described in more detail hereinafter, or as shown in the above described formulae (V) or (VI) in figure 6, in which case the metal complex is tetra-coordinated. The multidentate ligand may also be a tridentate Schiff base, in which case the metal complex is penta-coordinated.

The at least tetra-coordinated metal complex according to this first aspect of the invention preferably is a monometallic complex. Preferably the metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table. More preferably the said metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

Each of the metal, the radical R'''' , the ligand L^1 and the ligand L^2 may, independently from each other, be any of the above-mentioned metals or any of the above-mentioned groups with any of the substituents listed for such groups, including any of the individual meanings for such groups or substituents which are listed in the definitions given hereinabove. Preferably the non-anionic ligand L^2 has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. pentafluorophenyl. L^2 may also be a linear C_{1-7} alkyl such as methyl, or phenyl. Preferably the substituting radical R'''' also has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. 2,6-diisopropylphenyl, 2,6-ditert-butylphenyl or 2,6-diisopropyl-4-bromophenyl. Preferably the non-anionic unsaturated ligand L^1 also has constraint steric hindrance (such as, but not limited to, alkylaryl and alkylheteroaryl, e.g. xylyl, cumenyl or mesityl).

The at least tetra-coordinated metal complex according to this first aspect of the invention may for instance, but without limitation, be made according to the following procedure: a metal (e.g. thallium) salt of the multidentate ligand (e.g. the bidentate or tridentate Schiff base) is first reacted with a preferably bimetallic metal complex of the desired metal, more preferably a homobimetallic complex wherein the desired metal is coordinated with a non-anionic unsaturated ligand L^1 and at least one anionic ligand, such as $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(COD)]_2$ or $[RuCl_2(NBD)]_2$, wherein COD and NBD respectively mean cyclooctadiene and norbornadiene. After removal of the metal salt formed with the anionic ligand, e.g. thallium chloride, the intermediate complex produced, i.e. a complex wherein the desired metal is coordinated with a non-anionic unsaturated ligand L^1 , the multidentate ligand (e.g. the bidentate or tridentate Schiff base) and an anionic ligand, is reacted with a combination of the non-anionic ligand L^2 and an alkali or alkaline-earth metal, e.g. a C_{1-7} alkyllithium, a C_{1-7} alkylsodium, phenyllithium, or a Grignard reagent such as phenylmagnesium chloride, phenylmagnesium bromide or pentafluorophenylmagnesium chloride. Recovery of the desired at least tetra-coordinated metal complex of the invention is achieved by removal of the alkali or alkaline-earth metal salt formed with the anionic ligand, followed by purification using

conventional techniques. High yields of the pure at least tetra-coordinated metal complex of the invention may thus be achieved in a simple two-steps method.

In a second aspect, the present invention relates to a hexa-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- 5 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- 10 - at least one non-anionic bidentate ligand L³ being different from the multidentate ligand; and
- at most two anionic ligands L⁴.

Said hexa-coordinated metal complex is preferably a bimetallic complex wherein each metal is hexa-coordinated. The two metals may be the same or different. Preferably each metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table. More preferably each said metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

20 The multidentate ligand is preferably defined as in the first aspect of the invention, i.e. preferably is a bidentate or tridentate Schiff base. Preferably the substituting radical R^m has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. 2,6-diisopropylphenyl, 2,6-ditert-butylphenyl or 2,6-diisopropyl-4-bromophenyl. The non-anionic bidentate ligand L³ is preferably a polyunsaturated C₃₋₁₀ cycloalkenyl group such as, but not limited to, norbornadiene, cyclooctadiene, cyclopentadiene, cyclohexadiene, cycloheptadiene or cycloheptatriene, or a heteroaryl group such as defined hereinabove, for instance (but without limitation) a 1-hetero-2,4-cyclopentadiene such as pyrrole, furan or thiophene, or a fused-ring derivative thereof such as indole, or a six-membered heteroaromatic compound such as pyridine, pyridazine, pyrimidine, pyrazine, triazines or tetrazines, or a fused-ring derivative thereof such as quinoline, isoquinoline, cinnoline, phtalazine, quinazoline, quinoxaline, pyridopyrimidine or pteridine. Each anionic ligand L⁴ is preferably selected from the group consisting of C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryloxy, C₁₋₂₀ alkoxy carbonyl, C₁₋₇ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate, arylphosphonate, C₁₋₂₀ alkylammonium, arylammonium, 30 alkyldiketonate (e.g. acetylacetonate), aryldiketonate, halogen, nitro and cyano, each of the said groups being as defined above. When said hexa-coordinated metal complex is monometallic, it preferably has only one anionic ligand L⁴.

The hexa-coordinated metal complex according to this second aspect of the invention may for instance, but without limitation, be made in high yield and purity in a one-step procedure, wherein a metal (e.g. thallium) salt of the multidentate ligand (e.g. the bidentate or tridentate Schiff base) is 40

reacted with a preferably bimetallic metal complex of the desired metal, more preferably a homobimetallic complex wherein the desired metal is coordinated with a non-anionic bidentate ligand L^3 and at least one anionic ligand, such as $[RuCl_2L^3]_2$, e.g. $[RuCl_2(COD)]_2$ or $[RuCl_2(NBD)]_2$, wherein COD and NBD respectively mean cyclooctadiene and norbornadiene. After removal of the metal salt formed with the anionic ligand, e.g. thallium chloride, the desired hexa-coordinated metal complex may be purified using conventional techniques.

In a specific embodiment which is useful namely when the metal complex of this second aspect of the invention is to be used in the presence of water, it may be advantageous when one or more anionic ligands L^4 of said hexa-coordinated metal complex is (are) abstracted and replaced with a solvent S as a ligand. This anionic ligand abstraction and replacement may be effected for instance by treating, in the presence of the solvent S, the hexa-coordinated metal complex of this second aspect of the invention with an equivalent amount of a compound having the formula A-E, wherein E is a trimethylsilyl group or a metal such as silver, thus resulting in a modified hexa-coordinated metal complex being a cationic species having the solvent S as a ligand (in place of L^4) and being associated with an anion A. The treatment also results in the formation of a compound L^4E (e.g. silver chloride or chlorotrimethylsilane) which can be removed from the reaction mixture by conventional techniques. Suitable anions A for this purpose may be, but without limitation, selected from the group consisting of hexafluorophosphate, hexafluoroantimonate, hexafluoroarsenate, perchlorate, tetrafluoroborate, tetra(pentafluorophenyl)borate, alkylsulfonates wherein the alkyl group may be substituted with one or more halogen atoms, and arylsulfonates (e.g. toluenesulfonate). Suitable solvents S for coordinating with the metal in such a cationic species may be selected from the group consisting of protic solvents, polar aprotic solvents and non-polar solvents such as aromatic hydrocarbons, chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, esters, ketones, amides, and water.

In another specific embodiment, both the at least tetra-coordinated metal complex of the first aspect of the invention and the hexa-coordinated metal complex of the second aspect of the invention may have, as a multidentate ligand, a bidentate Schiff base having the above described formulae (V) or (VI) shown in figure 6, or one of the general formulae (IA) or (IB) referred to in figure 1, wherein:

- Z is selected from the group consisting of oxygen, sulphur, selenium, NR''' , PR''' , AsR''' and SbR''' , wherein R''' is a radical selected from the group consisting of hydrogen, C_{1-7} alkyl, C_{3-10} cycloalkyl, aryl and heteroaryl;
- R'' and R''' are each a radical independently selected from the group consisting of hydrogen, C_{1-6} alkyl, C_{3-8} cycloalkyl, aryl and heteroaryl, or R'' and R''' together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-7} alkyl, C_{1-7} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, alkylammonium and arylammonium; and
- R' is either as defined for R'' and R''' when included in a Schiff base having the general formula (IA) or, when included in a Schiff base having the general formula (IB), is selected

from the group consisting of C_{1-7} alkylene and C_{3-10} cycloalkylene, the said alkylene and cycloalkylene group being optionally substituted with one or more substituents R_5 .

In this specific embodiment, preferably R'' and R''' together form a phenyl group which may be substituted with one or more preferably branched alkyl groups such as isopropyl or tert-butyl. Also preferably, the substituting radical R''' has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. 2,6-diisopropylphenyl, 2,6-ditert-butylphenyl or 2,6-diisopropyl-4-bromophenyl. The class of bidentate Schiff bases having the general formula (IA) is well known in the art and may be made for instance by condensing a salicylaldehyde with a suitably substituted aniline. The class of bidentate Schiff bases having the general formula (IB) may be made for instance by condensing benzaldehyde with a suitably selected amino-alcohol such as o-hydroxyaniline (when Z is oxygen), an amino-thiol (when Z is sulphur), a diamine, (when Z is NR''''), an aminophosphine (when Z is PR''''), an aminoarsine (when Z is AsR'''') or an aminostilbine (when Z is SbR'''').

In a third aspect, this invention also provides a process for the radical polymerisation of a monomer in the presence, as a catalyst component, of a tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- two anionic ligands L^8 ;
- a non-anionic unsaturated ligand L^9 selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C_{4-20} cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C_{1-7} alkyl groups or with electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- a ligand L^{10} being a saturated aliphatic monoamine selected from primary amines, secondary amines, cyclic secondary amines and tertiary amines, or a secondary or tertiary diamine.

Within this third aspect of the invention, each anionic ligand L^8 is preferably selected from the group consisting of C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-7} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, alkylidicketonate (e.g. acetyl-acetonate), arylidicketonate, halogen, nitro and cyano, each of the said groups being as defined hereinabove. Preferably the non-anionic unsaturated ligand L^9 has constraint steric hindrance (such as, but not limited to, alkylaryl and alkylheteroaryl, e.g. xylyl, cumenyl or mesityl).

The monoamine ligand L^{10} may include one (primary amine), two (secondary amine) or even three (tertiary amine) saturated aliphatic groups such as C_{1-7} alkyl or C_{3-10} cycloalkyl (each of them as defined hereinabove, respectively) being attached to the nitrogen atom through a single bond or, in the case of aliphatic secondary amines, may be a saturated heterocyclic monoamine. Thus the ligand L^{10} may be represented by the general formula $NR_{17}R_{18}R_{19}$ wherein each of R_{17} , R_{18} and R_{19} is independently selected from the group consisting of hydrogen, C_{1-7} alkyl and C_{3-10} cycloalkyl, provided that at most two of R_{17} , R_{18} and R_{19} are hydrogen, or two of them may together form a

saturated heterocyclic group preferably having from 5 to 7 carbon atoms. Illustrative examples include, but are not limited to, methylamine, dimethylamine, ethylamine, diethylamine, isopropylamine, diisopropylamine, n-butylamine, isobutylamine, ter-butylamine, dibutylamine, cyclopentyl-amine, dicyclopentylamine, cyclohexylamine, dicyclohexylamine, triethylamine, triisopropylamine, tri-butylamine, methylethylamine, norbornylamine, adamantylamine, piperidine, 1-ethylpiperidine and 1,4-diazabicyclo-[2.2.2]octane. Suitable diamines include N,N'-dimethylethylenediamine and N,N,N',N'-tetramethylethylenediamine.

Within this third aspect of the invention, the tetra-coordinated metal complex used is preferably a monometallic complex wherein the metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table. More preferably the said metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

Within this third aspect of the invention, each of the metal, the anionic ligands L^8 , the non-anionic ligand L^9 and the ligand L^{10} may, independently from each other, be any of the above-mentioned metals or any of the above-mentioned groups with any of the substituents listed for such groups, including any of the individual meanings for such groups or substituents which are listed in the definitions given hereinabove.

The tetra-coordinated metal complex used within this third aspect of the invention may be prepared, by similarity with a procedure described by Carter et al. in *Polyhedron* (1993) 12:1123, by reacting two equivalents of the saturated monoamine L^{10} with one equivalent of a preferably bimetallic metal complex of the desired metal, more preferably a homobimetallic complex wherein the desired metal is coordinated with a non-anionic unsaturated ligand L^9 and two anionic ligands L^8 , such as (when the metal is ruthenium) $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(COD)]_2$ or $[RuCl_2(NBD)]_2$, wherein COD and NBD respectively mean cyclooctadiene and norbornadiene.

The radical polymerisation process of this third aspect of the invention is a living atom transfer radical polymerisation which is operated under the conditions (including concentration of growing radicals, initiator, solvent, temperature and the like) and is applicable to the monomers indicated below with respect to the sixth aspect of the invention. Unexpectedly, this radical polymerisation process proceeds at an enhanced rate when compared to the polymerisation of the same monomer under the same conditions in the combined presence of a chlorotriphenylphosphino ruthenium complex and of a primary, secondary, cyclic secondary or tertiary amine additive, as described by Hamasaki et al. in *Macromolecules* (2002) 35:2934-2940.

In a fourth aspect, the present invention provides a catalytic system comprising:

(a) as the main catalytic species, the hexa-coordinated metal complex of the second aspect of the invention (including the modified cationic species thereof having a solvent S as a ligand), or the tetra-coordinated metal complex used in the third aspect of the invention, or an at least tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium,

nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;

- a non-anionic unsaturated ligand L⁵ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₆ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- a ligand L⁶ being either an anionic ligand or a non-anionic ligand selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and

(b) one or more second catalyst components being selected from the group consisting of Lewis acid co-catalysts (b₁), catalyst activators (b₂) and initiators having a radically transferable atom or group (b₃).

Thus the latter alternative of the main catalytic species includes the metal complex of the first aspect of the invention (when L⁶ is a non-anionic ligand), but is not limited thereto since the ligand L⁶ may also be an anionic ligand preferably selected from the group consisting of C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₇ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkyl-phosphonate, arylphosphonate, C₁₋₂₀ alkyl-ammonium, arylammonium, alkyl diketone (e.g. acetylacetonate), aryl diketone, halogen, nitro and cyano. In a specific embodiment which is useful namely when the complex is to be used in the presence of water, it may be advantageous when the anionic ligand L⁶ is abstracted and replaced with a solvent S as a ligand. This anionic ligand abstraction and replacement may be effected for instance by treating, in the presence of the solvent S, the at least tetra-coordinated metal complex having the anionic ligand L⁶ with an equivalent amount of a compound having the formula A-E, wherein E is a trimethylsilyl group or a metal such as silver, thus resulting in a modified at least tetra-coordinated metal complex being a cationic species having the solvent S as a ligand (in place of L⁶) and being associated with an anion A. The treatment also results in the formation of a compound L⁶E (e.g. silver chloride or chlorotrimethylsilane) which can be removed from the reaction mixture by conventional techniques. Suitable anions A for this purpose may, but without limitation, be selected from the group consisting of hexafluorophosphate, hexafluoroantimonate, hexafluoroarsenate, perchlorate, tetrafluoroborate, tetra(pentafluoro-phenyl)borate, alkylsulfonates wherein the alkyl group may be substituted with one or more halogen atoms, and arylsulfonates (e.g. toluenesulfonate). Suitable solvents S for coordinating with the metal in such a cationic species may be selected from the group consisting of protic solvents, polar aprotic solvents and non-polar solvents such as aromatic hydrocarbons,

chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, esters, ketones, amides, and water.

When L^6 is a non-anionic ligand, it preferably has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. pentafluorophenyl. L^6 may also be methyl or phenyl. Preferably the substituting radical R''' also has constraint steric hindrance such as, but not limited to, tert-butyl, neopentyl and mono- or polysubstituted phenyl, e.g. 2,6-diisopropylphenyl, 2,6-ditert-butylphenyl or 2,6-diisopropyl-4-bromophenyl. Preferably the non-anionic unsaturated ligand L^5 also has constraint steric hindrance (such as, but not limited to, alkylaryl and alkylheteroaryl, e.g. xylyl, cumenyl or mesityl).

In the catalytic system of this fourth aspect of the invention, the second component (b) will be selected according to the kind of reaction to be catalyzed. For instance, a co-catalyst (b_1) may be useful for increasing the reaction rate of the ring opening metathesis polymerisation of cyclic olefins and may be selected, but without limitation, from the group consisting of boron trihalides; trialkylboron; triarylboron; organoaluminum compounds; magnesium halides; aluminum halides; titanium or vanadium trihalides or tetrahalides or tetraalkoxides, preferably titanium tetrachloride or tetrakispropoxytitanium; antimony and bismuth pentahalides. For instance a co-catalyst (b_1) may be an organoaluminum compound selected from the group consisting of tri-n-alkylaluminums; dialkylaluminum hydrides, trialkenylaluminums, alkylaluminum alkoxides, dialkylaluminum alkoxides, dialkylaluminum aryloxides and dialkyl-aluminum halides. A catalyst activator (b_2) may also be useful for increasing the reaction rate of the ring opening metathesis polymerisation of cyclic olefins (thus may be combined with a co-catalyst (b_1) such as above defined) and may be a diazo compound such as, but not limited to, ethyldiazoacetate and trimethylsilyldiazomethane.

On the other hand, an initiator having a radically transferable atom or group (b_3) is usually required, together with the main catalytic species, for performing the radical polymerisation of a monomer since an ATRP catalytic system is based on the reversible formation of growing radicals in a redox reaction between the metal component and an initiator.

Suitable initiators include those compounds having the general formula $R_{35}R_{36}R_{37}CX_1$ wherein:

- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
- R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene

group of 2 to 5 carbon atoms), COCl, OH, CN, C₂₋₂₀ alkenyl (preferably vinyl), C₂₋₂₀ alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C₂₋₂₀ alkenyl.

In these initiators, X₁ is preferably bromine, which provides both a higher reaction rate and a lower polymer polydispersity.

5 When an alkyl, cycloalkyl, or alkyl-substituted aryl group is selected for one of R₃₅, R₃₆ and R₃₇, the alkyl group may be further substituted with an X₁ group as defined above. Thus, it is possible for the initiator to serve as a starting molecule for branch or star (co)polymers. One example of such an initiator is a 2,2-bis(halomethyl)-1,3-dihalopropane (e.g. 2,2-bis(chloromethyl)-1,3-dichloropropane or 2,2-bis(bromomethyl)-1,3-dibromopropane), and a preferred example is where
10 one of R₃₅, R₃₆ and R₃₇ is phenyl substituted with from one to five C₁₋₆ alkyl substituents, each of which may independently be further substituted with a X₁ group (e.g. α,α' -dibromoxylene, hexakis(α -chloro- or α -bromomethyl)benzene). Preferred initiators include 1-phenylethyl chloride and 1-phenylethyl bromide, chloroform, carbon tetrachloride, 2-chloropropionitrile and C₁₋₇ alkyl
15 esters of a 2-halo-C₁₋₇ carboxylic acid (such as 2-chloropropionic acid, 2-bromopropionic acid, 2-chloroisobutyric acid, 2-bromo-isobutyric acid and the like). Another example of a suitable initiator is dimethyl-2-chloro-2,4,4-trimethylglutarate.

In a fifth aspect, the present invention also provides a supported catalyst, preferably for use in a heterogeneous catalytic reaction, comprising:

- 20 (a) a catalytically active metal complex being selected from the group consisting of the at least tetra-coordinated metal complexes of the first aspect of the invention, the hexa-coordinated metal complexes of the second aspect of the invention (including the modified cationic species thereof having a solvent S as a ligand and being associated with an anion A), or the tetra-coordinated metal complexes used in the third aspect of the invention, or a catalytic system according to the fourth aspect of
25 the invention, and
- (b) a supporting amount of a carrier suitable for supporting said catalytically active metal complex or catalytic system (a).

In such a supported catalyst, said carrier may be selected from the group consisting of porous inorganic solids (including silica, zirconia and alumino-silica), such as amorphous or paracrystalline
30 materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins such as polystyrene resins and derivatives thereof. Porous inorganic solids that may be used with the catalysts of the invention have an open microstructure that allows molecules access to the relatively large surface areas of these materials that enhance their catalytic and sorptive activity. These porous materials can be sorted into three
35 broad categories using the details of their microstructure as a basis for classification. These categories are the amorphous and paracrystalline supports, the crystalline molecular sieves and modified layered materials. The detailed differences in the microstructures of these materials manifest themselves as important differences in the catalytic and sorptive behavior of the materials, as well as in differences in various observable properties used to characterize them, such as their
40 surface area, the sizes of pores and the variability in those sizes, the presence or absence of X-ray

diffraction patterns and the details in such patterns, and the appearance of the materials when their microstructure is studied by transmission electron microscopy and electron diffraction methods. Amorphous and paracrystalline materials represent an important class of porous inorganic solids that have been used for many years in industrial applications. Typical examples of these materials are the amorphous silicas commonly used in catalyst formulations and the paracrystalline transitional aluminas used as solid acid catalysts and petroleum reforming catalyst supports. The term "amorphous" is used here to indicate a material with no long range order and can be somewhat misleading, since almost all materials are ordered to some degree, at least on the local scale. An alternate term that has been used to describe these materials is "X-ray indifferent". The microstructure of the silicas consists of 100-250 Angstrom particles of dense amorphous silica (Kirk-Othmer Encyclopedia of Chemical Technology, 3rd. ed., vol. 20, 766-781 (1982)), with the porosity resulting from voids between the particles.

Paracrystalline materials such as the transitional aluminas also have a wide distribution of pore sizes, but better defined X-ray diffraction patterns usually consisting of a few broad peaks. The microstructure of these materials consists of tiny crystalline regions of condensed alumina phases and the porosity of the materials results from irregular voids between these regions (K. Wefers and Chanakya Misra, "Oxides and Hydroxides of Aluminum", Technical Paper No 19 Revised, Alcoa Research Laboratories, 54-59 (1987)). Since, in the case of either material, there is no long range order controlling the sizes of pores in the material, the variability in pore size is typically quite high. The sizes of pores in these materials fall into a regime called the mesoporous range,, including, for example, pores within the range of about 15 to about 200 Angstroms.

In sharp contrast to these structurally ill-defined solids are materials whose pore size distribution is very narrow because it is controlled by the precisely repeating crystalline nature of the materials' microstructure. These materials are called "molecular sieves"-the most important examples of which are zeolites. Zeolites, both natural and synthetic, have been demonstrated in the past to have catalytic properties for various types of hydrocarbon conversion. Certain zeolitic materials are ordered, porous crystalline aluminosilicates having a definite crystalline structure as determined by X-ray diffraction, within which there are a large number of smaller cavities which may be interconnected by a number of still smaller channels or pores. These cavities and pores are uniform in size within a specific zeolitic material. Since the dimensions of these pores are such as to accept for adsorption molecules of certain dimensions while rejecting those of larger dimensions, these materials are known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties. Such molecular sieves, both natural and synthetic, include a wide variety of positive ion-containing crystalline silicates. These silicates can be described as a rigid three-dimensional framework of SiO_4 and Periodic Table Group IIIB element oxide, e.g., AlO_4 , in which the tetrahedra are cross-linked by the sharing of oxygen atoms whereby the ratio of the total Group IIIB element, e.g., aluminum, and Group IVB element, e.g., silicon, atoms to oxygen atoms is 1:2. The electrovalence of the tetrahedra containing the Group IIIB element, e.g., aluminum, is balanced by the inclusion in the crystal of a cation, for example, an alkali metal or an alkaline earth metal cation. This can be expressed wherein the ratio of the Group IIIB element, e.g., aluminum, to

the number of various cations, such as Ca, Sr, Na, K or Li, is equal to 1. One type of cation may be exchanged either entirely or partially with another type of cation utilizing ion exchange techniques in a conventional manner. By means of such cation exchange, it has been possible to vary the properties of a given silicate by suitable selection of the cation. Many of these zeolites have come to be designated by letter or other convenient symbols, as illustrated by zeolites A (U.S. Pat. No. 2,882,243); X (U.S. Pat. No. 2,882,244); Y (U.S. Pat. No. 3,130,007); ZK-5 (U.S. Pat. No. 3,247,195); ZK-4 (U.S. Pat. No. 3,314,752); ZSM-5 (U.S. Pat. No. 3,702,886); ZSM-11 (U.S. Pat. No. 3,709,979); ZSM-12 (U.S. Pat. No. 3,832,449); ZSM-20 (U.S. Pat. No. 3,972,983); ZSM-35 (U.S. Pat. No. 4,016,245); ZSM-23 (U.S. Pat. No. 4,076,842); MCM-22 (U.S. Pat. No. 4,954,325); MCM-35 (U.S. Pat. No. 4,981,663); MCM-49 (U.S. Pat. No. 5,236,575); and PSH-3 (U.S. Pat. No. 4,439,409). The latter refers to a crystalline molecular sieve composition of matter named PSH-3 and its synthesis from a reaction mixture containing hexamethyleneimine, an organic compound which acts as directing agent for synthesis of a layered MCM-56. A similar composition, but with additional structural components, is taught in European Patent Application 293,032. Hexamethyleneimine is also taught for use in synthesis of crystalline molecular sieves MCM-22 in U.S. Pat. 4,954,325; MCM-35 in U.S. Pat. No. 4,981,663; MCM-49 in U.S. Pat. 5,236,575; and ZSM-12 in U.S. Pat. No. 5,021,141. A molecular sieve composition SSZ-25 is taught in U.S. Pat. No. 4,826,667 and European Patent Application 231,860, said zeolite being synthesized from a reaction mixture containing an adamantane quaternary ammonium ion. Molecular sieve material being selected from the group consisting of zeolites REY, USY, REUSY, dealuminated Y, ultrahydrophobic Y, silicon-enriched dealuminated Y, ZSM-20, Beta, L, silicoaluminophosphates SAPO-5, SAPO-37, SAPO-40, MCM-9, metalloaluminophosphate MAPO-36, aluminophosphate VPI-5 and mesoporous crystalline MCM-41 are suitable for including into a supported catalyst of this invention.

MCM-41 has a uniform structure exhibiting hexagonal arrangement of straight mesopores, such as honeycomb, and has a specific surface area of about 1,000 m²/g as measured by ordinary BET.

Existing molecular sieves have been produced by using inorganic or organic cations as templates, whereas those mesoporous molecular sieves are synthesized through a liquid crystal template pathway by using surfactants as templates. These mesoporous molecular sieves have the advantage that their pore sizes can be adjusted in a range of 1.6 to 10 nm by controlling the kinds of surfactants or synthetic conditions employed during the production process. The following mesoporous molecular sieves are also suitable for including into a supported catalyst of this invention:

- mesoporous molecular sieves designated as SBA-1, -2 and 3 reported in *Science* (1995) 268:1324. Their channels are regularly arranged, while the constituent atoms show an arrangement similar to that of amorphous silica. Mesoporous molecular sieves have regularly arranged channels larger than those of existing zeolites, thus enabling their application to adsorption, isolation or catalyst conversion reactions of relatively large molecules;

- a family of high quality, hydrothermally stable and ultra large pore size mesoporous silicas by using amphiphilic block copolymers in acidic media as disclosed by U.S. Patent No. 6,592,764. One member of the family, SBA-15, has a highly ordered, two-dimensional hexagonal honeycomb, hexagonal cage or cubic cage mesostructure. Calcination at 500 °C yields porous structures with high BET surface areas of 690 to 1,040 m²/g, and pore volumes up to 2.5 cm³/g, ultra large d(100) spacings of 7.45 - 45 nm, pore sizes from 4.6 - 50 nm and silica wall thicknesses of 3.1 - 6.4 nm. SBA-15 can be readily prepared over a wide range of specific pore sizes and pore wall thicknesses at low temperature (35 - 80 °C) using a variety of commercially available, non-toxic and biodegradable amphiphilic block copolymers, including triblock polyoxyalkylenes;
 - U.S. Patent No. 6,630,170 discloses a mesoporous composition prepared from a mixture comprising hydrochloric acid, vitamin E and a silica source, wherein said vitamin E functions as a templating molecule, and said mesoporous composition exhibits uniform pore size; and
 - U.S. Patent No. 6,669,924 discloses a mesoporous zeolitic material having a stereoregular arrangement of uniformly-sized mesopores with diameters ranging from 2 to 50 nm and walls having a thickness of at least 4 nm and a microporous nanocrystalline structure, the mesopore walls having a stereoregular arrangement of uniformly-sized micropores with diameters less than 1.5 nm.
- Certain layered materials, which contain layers capable of being spaced apart with a swelling agent, may be pillared to provide materials having a large degree of porosity. Examples of such layered materials include clays. Such clays may be swollen with water, whereby the layers of the clay are spaced apart by water molecules. Other layered materials are not swellable with water, but may be swollen with certain organic swelling agents such as amines and quaternary ammonium compounds. Examples of such non-water swellable layered materials are described in U.S. Pat. No. 4,859,648 and include layered silicates, magadiite, kenyaite, trititanates and perovskites. Another example of a non-water swellable layered material, which can be swollen with certain organic swelling agents, is a vacancy-containing titanometallate material, as described in U.S. Pat. No. 4,831,006. Once a layered material is swollen, the material may be pillared by interposing a thermally stable substance, such as silica, between the spaced apart layers. The aforementioned U.S. Pat. Nos. 4,831,006 and 4,859,648 describe methods for pillaring the non-water swellable layered materials described therein and are incorporated herein by reference for definition of pillaring and pillared materials. Other patents teaching pillaring of layered materials and the pillared products include U.S. Pat. Nos. 4,216,188; 4,248,739; 4,176,090; and 4,367,163; and European Patent Application 205,711. The X-ray diffraction patterns of pillared layered materials can vary considerably, depending on the degree that swelling and pillaring disrupt the otherwise usually well-ordered layered microstructure. The regularity of the microstructure in some pillared layered materials is so badly disrupted that only one peak in the low angle region on the X-ray diffraction pattern is observed, at a d-spacing corresponding to the interlayer repeat in the pillared material. Less disrupted materials may show several peaks in this region that are generally

orders of this fundamental repeat. X-ray reflections from the crystalline structure of the layers are also sometimes observed. The pore size distribution in these pillared layered materials is narrower than those in amorphous and paracrystalline materials but broader than that in crystalline framework materials.

5 In a sixth aspect, the present invention provides the use of a hexa-coordinated metal complex according to the second aspect of the invention (including the modified cationic species thereof having a solvent S as a ligand and being associated with an anion A) or an at least tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- a non-anionic unsaturated ligand L⁵ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₆ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- a ligand L⁶ being either an anionic ligand or a non-anionic ligand selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide,

or a tetra-coordinated or penta-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- a tetradentate ligand comprising two Schiff bases, and
- optionally a solvent ligand S, the said metal complex then being associated with an anion A, said solvent S and said anion A being as defined hereinabove,

or a tetra-coordinated or penta-coordinated metal complex comprising:

- at least one bidentate phosphine ligand, and
- at least one other ligand being selected from the group consisting of solvent ligands S, in which case the complex is a cationic species associated with an anion A, said solvent S and said anion A being as defined hereinabove; anionic ligands and non-anionic ligands,

as a catalytic component in olefin metathesis (the latter being as explained in the background of the invention or as defined in <http://www.ilpi.com/organomet/olmetathesis.html>), in particular the ring-opening metathesis polymerisation of cyclic olefins, or in acetylene metathesis (the latter being as defined in <http://www.ilpi.com/organomet/acmetathesis.html> and involving a metallacyclobutadiene intermediate) or in a reaction involving the transfer of an atom or group to an

ethylenically or acetylenically unsaturated compound or another reactive substrate such as, but not limited to, saturated hydrocarbons, aldehydes, ketones, alcohols, alkyl halides and the like. Briefly, acetylene metathesis may be referred to herein as a reaction in which all carbon-carbon triple bonds in a mixture of alkynes are cut and then rearranged in a statistical fashion.

5 An atom or group transfer reaction usually comprises the step of reacting the said ethylenically or acetylenically unsaturated compound or other reactive substrate with a second reactive substrate under suitable reaction conditions and in the presence of a suitable catalytic component, the second reactive substrate being a suitable donor for the atom or group to be transferred. In this sixth aspect of the invention, the catalytic component is such as above defined, i.e. namely
10 includes the metal complexes of both the first and second aspects of the invention but is not limited thereto.

More specifically, the said atom or group transfer reactions (which will be detailed below) may be, but without limitation, selected from the group consisting of:

- 15 - atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
- atom transfer radical addition (the latter being as explained in the background of the invention), e.g. the addition of a polyhalomethane having the formula CX_nH_{4-n} , wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to produce the corresponding saturated polyhalogenated adduct, including for instance the
20 addition of carbon tetrachloride or chloroform onto an α -olefin;
- vinylation reaction, i.e. the reaction of a mono- or di-alkyne (e.g. phenylacetylene or 1,7-octadiyne) with a monocarboxylic acid (e.g. formic acid or acetic acid) or dicarboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti- Markovnikov adducts or mixtures thereof;
- 25 - cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
- quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
- epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
- oxidation of organic compounds including the oxidation of saturated hydrocarbons (such
30 as, but not limited to, methane) for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
- cyclopropanation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
- 35 - hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds;
- hydrosilylation of olefins for producing saturated silanes, or alkynes for producing
40 unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;

- aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units;
- hydroamidation of olefins for producing saturated amides;
- hydrogenation of olefins for producing alkanes, and hydrogenation of ketones for producing alcohols;
- aminolysis and hydroamination of olefins for producing saturated primary or secondary amines, and hydroamination of alkynes for producing unsaturated amines;
- isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
- Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
- hydroboration of olefins for producing alkylboranes and trialkylboranes;
- hydride reduction of aldehydes and ketones for producing alcohols;
- aldol condensation of saturated carboxyl compounds (aldehydes or ketones) for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds (aldehydes or ketones);
- Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
- Robinson annulation, i.e. Michael addition followed by an intramolecular aldol condensation, of a ketone onto an α,β -unsaturated carboxyl compound for producing saturated polycyclic carboxyl compounds being suitable intermediates for steroids and other natural products containing six-membered rings;
- Heck reactions, i.e. the reaction of an aryl halide or a 1-hetero-2,4-cyclopentadiene (or a benzo-fused derivative thereof) with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
- codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
- hydroxylation of olefins for producing alcohols;
- alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones;
- Diels-Alder reactions such as, but not limited to, the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbomenes;
- Suzuki-Miyaura cross-coupling reactions;
- silylmatalation of unsaturated compounds, particularly olefins and carbonyl compounds; and
- carbometalation reactions of silyl cyanides and allyl silanes with carbonyl compounds and olefins.

Each of the above organic synthesis reactions, which will be described in more detail hereinafter, is known *per se*. For further details on each type of reaction, reference may be made for instance to

K. Vollhardt and N. Schore, *Organic chemistry, structure and function* (1999) by W.H. Freeman (3rd edition) and to B. Cornils and A. Herrmann, *Applied homogeneous catalysis with organometallic compounds* (2000) by Wiley.

Each organic synthesis reaction of this sixth aspect of the invention may be conducted in a continuous, semi-continuous, or batch manner and may involve a liquid and/or gas recycling operation as desired. The manner or order of addition of the reactants, catalyst, and solvent are usually not critical. Each organic synthesis reactions may be carried out in a liquid reaction medium that contains a solvent for the active catalyst, preferably one in which the reactants, including catalyst, are substantially soluble at the reaction temperature.

In a first embodiment of this sixth aspect of the invention, the said reaction is an olefin metathesis reaction for transforming a first olefin into at least one second olefin or into a linear olefin oligomer or polymer or into a cyclo-olefin. The invention thus relates to a method for performing an olefin metathesis reaction comprising contacting at least one first olefin with the catalytic component, optionally supported on a suitable carrier such as described hereinabove with reference to the fifth aspect of the invention. The high activity of the metal complexes of this invention cause these compounds to coordinate with, and catalyze metathesis reactions between, many types of olefins. Exemplary olefin metathesis reactions enabled by the metal complexes of the present invention include, but are not limited to, RCM of acyclic dienes, cross metathesis reactions, de-polymerization of olefinic polymers and, more preferably, ROMP of strained cyclic olefins. In particular, the catalytic components of this invention may catalyze ROMP of unsubstituted, monosubstituted and disubstituted strained mono-, bi- and polycyclic olefins with a ring size of at least 3, preferably 3 to 5, atoms; examples thereof include norbornene, cyclobutene, norbornadiene, cyclopentene, dicyclopentadiene, cycloheptene, cyclooctene, 7-oxanorbornene, 7-oxanorbornadiene, cyclooctadiene, cyclododecene, mono- and disubstituted derivatives thereof, especially derivatives wherein the substituent may be C₁₋₇ alkyl, cyano, diphenylphosphine, trimethylsilyl, methylaminomethyl, carboxylic acid or ester, trifluoromethyl, maleic ester, maleimido and the like, such as disclosed in U.S. Patent No. 6,235,856, the content of which is incorporated herein in its entirety. The invention also contemplates ROMP of mixtures of two or more such monomers in any proportions. Further examples include water-soluble cyclic olefins such as exo-N-(N',N',N'-trimethylammonio)ethyl-bicyclo[2.2.1] hept-5-ene-2,3-dicarboximide chloride or exo-N-(N',N',N'-trimethylammonio)ethyl-bicyclo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboximide chloride. As is well known to the skilled person, olefins such as cyclohexenes which have little or no ring strain cannot be polymerized because there is no thermodynamic preference for polymer versus monomer.

ROMP of the invention may be carried out in an inert atmosphere for instance by dissolving a catalytic amount of the catalytic component in a suitable solvent and then adding one or more of the said strained cyclic olefins, optionally dissolved in the same or another solvent, to the catalyst solution, preferably under agitation. Because a ROMP system is typically a living polymerisation process, two or more different strained cyclic olefins may be polymerised in subsequent steps for making diblock and triblock copolymers, thus permitting to tailor the properties of the resulting

material, provided that the ratio of chain initiation and chain propagation is suitably selected. Solvents that may be used for performing ROMP include all kinds of organic solvents such as protic solvents, polar aprotic solvents and non-polar solvents, as well as supercritical solvents such as carbon dioxide (while performing ROMP under supercritical conditions) and aqueous solvents, which are inert with respect to the strained cyclic olefin and the catalytic component under the polymerization conditions used. More specific examples of suitable organic solvents include ethers (e.g. dibutyl ether, tetrahydrofuran, dioxane, ethylene glycol monomethyl or dimethyl ether, ethylene glycol monoethyl or diethyl ether, diethylene glycol diethyl ether or triethylene glycol dimethyl ether), halogenated hydrocarbons (e.g. methylene chloride, chloroform, 1,2-dichloroethane, 1,1,1-trichloroethane or 1,1,2,2-tetrachloroethane), carboxylic acid esters and lactones (e.g. ethyl acetate, methyl propionate, ethyl benzoate, 2-methoxyethyl acetate, γ -butyrolactone, δ -valerolactone or pivalolactone), carboxylic acid amides and lactams (e.g. N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, tetramethylurea, hexamethylphosphoric acid triamide, γ -butyrolactam, ϵ -caprolactam, N-methylpyrrolidone, N-acetylpyrrolidone or N-methylcaprolactam), sulfoxides (e.g. dimethyl sulfoxide), sulfones (e.g. dimethyl sulfone, diethyl sulfone, trimethylene sulfone or tetramethylene sulfone), aliphatic and aromatic hydrocarbons (e.g. petroleum ether, pentane, hexane, cyclohexane, methylcyclohexane, benzene, chlorobenzene, o-dichlorobenzene, 1,2,4-trichlorobenzene, nitrobenzene, toluene or xylene), and nitriles (e.g. acetonitrile, propionitrile, benzonitrile or phenylacetonitrile).

When water or an aqueous mixture is selected as the solvent, it is preferable to use a cationic metal complex species as the catalytic component, the said cationic species being associated with an anion A as described hereinabove.

The solubility of the polymer formed by ROMP will depend upon the choice of the strained cyclic olefin, the choice of the solvent and the molecular weight and concentration of the polymer obtained. When the strained cyclic olefin is polyunsaturated (e.g. dicyclopentadiene or norbornadiene), the polymer obtained may often be insoluble, whatever the solvent used. Polymerisation temperatures may range from about 0°C to about 120°C, preferably 20°C to 85°C, also depending upon the strained cyclic olefin and the solvent. The duration of polymerisation may be at least about 1 minute, preferably at least 5 minutes, and more preferably at least 30 minutes; the duration of polymerisation may be at most about 24 hours (although longer times may be used at the expense of economic conditions), preferably at most about 600 minutes, and even below 60 minutes. The molar ratio of the strained cyclic olefin to the catalytic component of the invention is not critical and, depending upon the olefin to be polymerised, may be at least about 100, preferably at least 250, more preferably at least 500. The said molar ratio is usually at most about 1,000,000, preferably at most 300,000 and more preferably at most 50,000. Before the polymer formed solidifies in the reactor or mold or, at will, when a desired molecular weight of the polymer has been achieved (as may be controlled for instance by monitoring reactor temperature and/or reaction mixture viscosity), an oxidation inhibitor and/or a terminating or chain-transfer agent may be added to the reaction mixture, if needed. The choice of the terminating or chain-transfer agent used is not critical to this invention, provided that the said terminating agent reacts with the catalytic

component and produces another species which is inactive, i.e. not able to further propagate the polymerisation reaction, under the prevailing conditions (e.g. temperature). For instance, adding a molar excess (with respect to the catalytic component) of a carbonyl compound to the reaction mixture is able to produce a metal oxo and an olefin (or polymer) capped with the former carbonyl functionality; the cleaved polymer can then be separated from the catalyst by precipitation with methanol. Another way of cleaving the polymer from the catalyst may be by the addition of a vinylalkylether. Alternatively, reaction with several equivalents of a chain-transfer agent such as a diene is another way of cleaving the polymer chain, which method does not deactivate the catalytic component, permitting additional monomer to be polymerised, however possibly at the risk of broadening molecular weight distribution.

Because the metal complexes of this invention are stable in the presence of various functional groups, they may be used to catalyze a wide variety of olefins under a wide variety of process conditions. In particular the olefinic compound to be converted by a metathesis reaction may include one or more, preferably at most 2, functional atoms or groups, being for instance selected from the group consisting of hydroxyl, thiol (mercapto), ketone, aldehyde, ester (carboxylate), thioester, cyano, cyanato, epoxy, silyl, silyloxy, silanyl, siloxazanyl, boronato, boryl, stannyl, disulfide, carbonate, imine, carboxyl, amine, amide, carboxyl, isocyanate, thioisocyanate, carbodiimide, ether (preferably C₁₋₂₀ alkoxy or aryloxy), thioether (preferably C₁₋₂₀ thioalkoxy or thioaryloxy), nitro, nitroso, halogen (preferably chloro), ammonium, phosphonate, phosphoryl, phosphino, phosphanyl, C₁₋₂₀ alkylsulfanyl, arylsulfanyl, C₁₋₂₀ alkylsulfonyl, arylsulfonyl, C₁₋₂₀ alkylsulfinyl, arylsulfinyl, sulfonamido and sulfonate (preferably toluenesulfonate, methanesulfonate or trifluoromethanesulfonate). The said olefin functional atom or group may be either part of a substituting group of the olefin or part of the carbon chain of the olefin.

The metal complexes of this invention are also useful components for catalyzing, at relatively low temperatures (from about 20°C to 80°C), in the presence or absence of a solvent, the ring-closing metathesis of acyclic dienes such as, for instance, diallylic compounds (diallyl ether, diallyl thioether, diallyl phthalate, diallylamino compounds such as diallylamine, diallylamino phosphonates, diallyl glycine esters), 1,7-octadiene, substituted 1,6-heptadienes and the like.

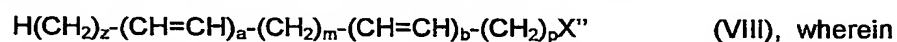
The metal complexes of this invention may also be used as catalytic components for the preparation of telechelic polymers, i.e. macromolecules with one or more reactive end-groups which are useful materials for chain extension processes, block copolymer synthesis, reaction injection moulding, and polymer network formation. An example thereof is hydroxyl-telechelic polybutadiene which may be obtained from 1,5-cyclooctadiene, 1,4-diacetoxy-cis-2-butene and vinyl acetate. For most applications, a highly functionalized polymer, i.e. a polymer with at least two functional groups per chain, is required. The reaction scheme for a telechelic polymer synthesis via ring opening metathesis polymerisation is well known to those skilled in the art: in such a scheme, acyclic olefins act as chain-transfer agents in order to regulate the molecular weight of the telechelic polymer produced. When α,ω -bifunctional olefins are used as chain-transfer agents, truly bi-functional telechelic polymers can be synthesized.

According to the sixth aspect of the invention, olefin coupling may be performed by cross-metathesis comprising the step of contacting a first olefinic compound with such a metal complex in the presence of a second olefin or functionalized olefin. The said first olefinic compound may be a diolefin or a cyclic mono-olefin with a ring size of at least 3 atoms, and the said metathesis cross-coupling is preferably performed under conditions suitable for transforming said cyclic mono-olefin into a linear olefin oligomer or polymer, or said diolefin into a mixture of a cyclic mono-olefin and an aliphatic alpha-olefin.

Depending upon the selection of the starting substrates for the olefin metathesis reaction and the desired organic molecule to be produced, the olefin metathesis reaction can yield a very wide range of end-products including biologically active compounds. For instance the reaction may be for transforming a mixture of two dissimilar olefins, at least one of which is an alpha-olefin, selected from (i) cyclodienes containing from 5 to 12 carbon atoms and (ii) olefins having the formula:



into an unsaturated biologically active compound having the formula:



a is an integer from 0 to 2; b is selected from 1 and 2; c is selected from 0 and 1; m and p are such that the hydrocarbon chain in formula (VIII) contains from 10 to 18 carbon atoms; r and t are such that the combined total of carbon atoms in the hydrocarbon chains of the two dissimilar olefins of formula (VII) is from 12 to 40; z is an integer from 1 to 10, and X, X' and X'' are atoms or groups each independently selected from hydrogen, halogen, methyl, acetyl, -CHO and -OR₁₂, wherein R₁₂ is selected from hydrogen and an alcohol protecting group selected from the group consisting of tetrahydropyranyl, tetrahydrofuranyl, tert-butyl, trityl, ethoxyethyl and SiR₁₃R₁₄R₁₅ wherein R₁₃, R₁₄ and R₁₅ are each independently selected from C₁₋₇ alkyl groups and aryl groups.

The said unsaturated biologically active compound having the formula (VIII) may be a pheromone or pheromone precursor, an insecticide or a insecticide precursor, a pharmaceutically active compound or a pharmaceutical intermediate, a fragrance or a fragrance precursor. A few examples of the said unsaturated biologically active compounds include 1-chloro-5-decene, 8,10-dodecadienol, 3,8,10-dodecatrienol, 5-decenyl acetate, 11-tetradecenylacetate, 1,5,9-tetradecatriene and 7,11-hexadecadienyl acetate. The latter is a pheromone commercially available under the trade name Gossyplure, useful in pest control by effectively disrupting the mating and reproductive cycles of specifically targeted insect species, which may be produced from 1,5,9-tetradecatriene, the latter being obtainable from cyclooctadiene and 1-hexene according to the present invention.

When performing the olefin metathesis reaction of the invention, although in most cases the said reaction proceeds very quickly, it may be advantageous for a few specific olefins, in order to improve the reaction rate and/or yield, to further contact the olefin with a Lewis acid co-catalyst (b₁) and/or a catalyst activator (b₂). The Lewis acid co-catalyst (b₁) may be selected from the group consisting of boron trihalides; trialkylboron; triarylboron; organoaluminum compounds; magnesium halides; aluminum halides; titanium or vanadium halides, preferably titanium tetrachloride; antimony and bismuth pentahalides. For instance the Lewis acid co-catalyst (b₁) may be an

organoaluminum compound selected from the group consisting of tri-n-alkylaluminums; dialkylaluminum hydrides, trialkenylaluminums, alkylaluminum alkoxides, dialkylaluminum alkoxides, dialkylaluminum aryloxides and dialkylaluminum halides. The catalyst activator (b_2) may be for instance a diazo compound such as, but not limited to, ethyldiazoacetate and trimethylsilyldiazomethane.

At the opposite, ring-opening metathesis polymerization (ROMP) reactions using the catalytic components of the invention may proceed so quickly for olefinic monomers such as dicyclopentadiene or oligomers thereof (i.e. Diels-Alder adducts formed with about 1 to 20 cyclopentadiene units) or mixtures thereof with strained monocyclic or polycyclic fused olefins (e.g. as defined in U. S. Patent No. 6,235,856, the content of which is incorporated herein by reference) that polymerization control could become a problem in the absence of appropriate measures. This kind of problem is likely to occur during the molding of thermoset polymers wherein a liquid olefin monomer and a catalyst are mixed and poured, cast or injected into a mold and wherein on completion of polymerization (i.e. "curing" of the article) the molded part is removed from the mold before any post cure processing that may be required, such as in the Reaction Injection Molding ("RIM") technique. It is well known that the ability to control reaction rates, i.e. the pot life of the reaction mixture, becomes more important in the molding of larger parts using this technique. Using the catalytic components of this invention, extending the pot life and/or controlling the rate of an olefin metathesis polymerisation reaction may be effected in different ways, such as increasing the catalyst/olefin ratio and/or adding a polymerization retardant to the reaction mixture. Moreover this can be achieved by an improved embodiment comprising:

- (a) a first step of contacting the olefin metathesis catalytic component (optionally supported) of the invention with an olefin in a reactor at a first temperature at which the said olefin metathesis-catalytic component is substantially unreactive (inactive), and
- (b) a second step of bringing the reactor temperature (e.g. heating the contents of said reactor) up to a second temperature above the said first temperature, at which said catalytic component is active, until completion of polymerisation.

In a more specific version of this improved embodiment, heat activation occurs in bursts rather than continuously, e.g. by repeating the sequence of steps (a) and (b).

Within the said controlled polymerization method, it should be understood that the non-reactivity of the catalytic component in the first step depends not only on the first temperature but also on the nature of the olefin(s) used in the said RIM technique and on the olefin/catalytic component ratio. Preferably the first temperature is about 20°C but, for specific olefins or specific olefin/catalytic component ratios, it may even be suitable to cool the reaction mixture below room temperature, e.g. down to about 0°C. The second temperature is preferably above 40°C and may be up to about 90°C.

ROMP using the catalytic components of this invention readily achieve linear or crosslinked polymers of the above-mentioned strained cyclic olefins, such as polynorbornenes and polydicyclopentadienes, with well controlled characteristics, i.e. average molecular weight and

molecular weight distribution (polydispersity). In particular, norbornene polymers with an average molecular weight ranging from about 200,000 to 2,000,000 and a molecular weight distribution (polydispersity) from about 1.1 to 2.2 may be prepared. Polymerisation, in particular when performed in a mold such as in the RIM technique, may occur in the presence of one or more
5 formulation auxiliaries, such as antistatics, antioxidants, ceramics, light stabilizers, plasticizers, dyes, pigments, fillers, reinforcing fibers, lubricants, adhesion promoters, viscosity-enhancing agents and demolding agents, all said auxiliaries being well known in the art.

Depending upon the specific reaction involved in this sixth aspect of this invention, and especially when the said reaction is ROMP of strained cyclic olefins, reaction may also
10 advantageously be performed under visible light or ultra-violet light irradiation, e.g. using a source of visible light or ultra-violet light being able to deliver sufficient energy to the reaction system.

In another embodiment of the sixth aspect of the present invention, the catalytic component is used for the atom transfer radical addition (ATRA) reaction of a polyhalogenated alkane $CXCl_3$, wherein X is hydrogen, C_{1-7} alkyl, phenyl or halogen, onto an olefin or diolefin. Such reaction is
15 preferably performed in the presence of an organic solvent, in a molar excess of the polyhalogenated alkane, and within a temperature range between about 30° and 100°C. Suitable examples of the polyhalogenated alkanes are carbon tetrachloride, chloroform, trichlorophenylmethane and carbon tetrabromide. Examples of suitable olefins for this radical addition reaction include internal and cyclic olefins as well as terminal olefins having the formula
20 $RR'C=CH_2$, wherein R and R' may be each independently selected from hydrogen, C_{1-7} alkyl, phenyl and carboxylic acid or ester, e.g. vinylaromatic monomers such as styrene or vinyltoluene, α,β -ethylenically unsaturated acid esters such as C_{1-7} alkyl acrylates and methacrylates, acrylonitrile and the like.

In another embodiment of the sixth aspect of the present invention, the catalytic component is
25 used for the atom or group transfer radical polymerization (ATRP) of one or more radically (co)polymerizable monomers. It is critical to the success of the living/controlled radical polymerisation contemplated in this embodiment to achieve rapid exchange between growing radicals present at low stationary concentrations (in a range of from about 10^{-8} mole/l to 10^{-6} mole/l) and dormant chains present at higher concentrations (typically in a range of from about 10^{-4} mole/l
30 to 1 mole/l). It may therefore be desirable to match the respective amounts of the catalytic component of the invention and of the radically (co)polymerizable monomer(s) in such a way that these concentration ranges are achieved. If the concentration of growing radicals exceeds about 10^{-6} mole/l, there may be too many active species in the reaction, which may lead to an undesirable increase in the rate of side reactions (e.g. radical-radical quenching, radical abstraction from
35 species other than the catalyst system, and so on). If the concentration of growing radicals is less than about 10^{-8} mole/l, the polymerisation rate may be undesirably slow. Similarly, if the concentration of dormant chains is less than about 10^{-4} mole/l, the molecular weight of the polymer produced may increase dramatically, thus leading to a potential loss of control of its polydispersity. On the other hand, if the concentration of dormant species is greater than 1 mole/l, the molecular
40 weight of the reaction product may likely become too small and result in the properties of an

oligomer with no more than about 10 monomeric units. In bulk, a concentration of dormant chains of about 10^{-2} mole/l provides a polymer having a molecular weight of about 100,000 g/mole.

The various catalytic components of the present invention are suitable for the radical polymerisation of any radically polymerizable, ethylenically or acetylenically unsaturated compound, including acrylic acid, methacrylic acid, acrylic acid esters, methacrylic acid esters, acrylic acid amides, methacrylic acid amides, imides (such as N-cyclohexylmaleimide and N-phenylmaleimide), styrenes, dienes or mixtures thereof. By providing the said compounds in a single step or in a multi-steps procedure, they are able to provide controlled copolymers having various structures, including block, random, gradient, star-shaped, graft, comb-shaped, hyperbranched and dendritic (co)polymers of various monomer compositions and, consequently, having tailored properties such as heat resistance, scratch resistance, solvent resistance, etc.

More specifically, monomers suitable for ATRP include those of the formula $R_{31}R_{32}C\equiv C R_{33}R_{34}$ wherein:

- R_{31} and R_{32} are independently selected from the group consisting of hydrogen, halogen, CN, CF_3 , C_{1-20} alkyl (preferably C_{1-6} alkyl), α,β -unsaturated C_{2-20} alkynyl (preferably acetylenyl), α,β -unsaturated C_{2-20} alkenyl (preferably vinyl) optionally substituted (preferably at the α position) with a halogen, C_{3-8} cycloalkyl, phenyl optionally bearing 1 to 5 substituents,
- R_{33} and R_{34} are independently selected from the group consisting of hydrogen, halogen (preferably fluorine or chlorine), C_{1-6} alkyl and $COOR_{35}$ (where R_{35} is selected from hydrogen, an alkali metal, or C_{1-6} alkyl), and
- at least two of R_{31} , R_{32} , R_{33} and R_{34} are hydrogen or halogen.

Accordingly, vinyl heterocyclic monomers suitable for ATRP in this embodiment of the sixth aspect of the invention include, but are not limited to, 2-vinyl pyridine, 6-vinyl pyridine, 2-vinyl pyrrole, 5-vinyl pyrrole, 2-vinyl oxazole, 5-vinyl oxazole, 2-vinyl thiazole, 5-vinyl thiazole, 2-vinyl imidazole, 5-vinyl imidazole, 3-vinyl pyrazole, 5-vinyl pyrazole, 3-vinyl pyridazine, 6-vinyl pyridazine, 3-vinyl isoxazole, 3-vinyl isothiazoles, 2-vinyl pyrimidine, 4-vinyl pyrimidine, 6-vinyl pyrimidine, and any vinyl pyrazine, the most preferred being 2-vinyl pyridine.

Other preferred monomers include:

- (meth)acrylic esters of C_{1-20} alcohols,
- acrylonitrile,
- cyanoacrylic esters of C_{1-20} alcohols,
- dihydromalonate diesters of C_{1-7} alcohols,
- vinyl ketones, and
- styrenes optionally bearing a C_{1-7} alkyl group on the vinyl moiety (preferably at the α carbon atom) and/or bearing from 1 to 5 substituents on the phenyl ring, said substituents being selected from the group consisting of C_{1-7} alkyl, C_{1-7} alkenyl (preferably vinyl or allyl), C_{1-7} alkynyl (preferably acetylenyl), C_{1-7} alkoxy, halogen, nitro, carboxy, C_{1-7} alkoxy carbonyl, hydroxy protected with a C_{1-7} acyl group, cyano and phenyl.

The most preferred monomers for ATRP are methyl acrylate, methyl methacrylate, butyl acrylate, 2-ethylhexyl acrylate, acrylonitrile, maleimide and styrene.

In this embodiment, the catalytic component of the invention is more preferably used in combination with one or more initiators having a radically transferable atom or group, since an ATRP catalytic system is based on the reversible formation of growing radicals in a redox reaction between the metal component and an initiator. Suitable initiators may be selected from the group consisting of compounds having the general formula $R_{35}R_{36}R_{37}CX_1$, wherein:

- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from the group consisting of C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl or allyl), phenyl optionally substituted with 1 to 5 substituents selected from the group consisting of halogen and C_{1-7} alkyl, and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present in the said X_1 , the two R_{39} groups may be joined together to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition above), and
- R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-7} alkyl), C_{3-10} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition above), $COCl$, OH , CN , C_{2-20} alkenyl (preferably vinyl), C_{2-20} alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C_{2-20} alkenyl.

In the latter initiators X_1 is preferably bromo which provides both a higher reaction rate and a lower polymer polydispersity.

When an alkyl, cycloalkyl, or alkyl-substituted aryl group is selected for one of R_{35} , R_{36} and R_{37} , the alkyl group may be further substituted with a group X_1 such as defined above, in particular a halogen atom. Thus, it is possible for the initiator to serve as a starting molecule for branched, comb-shaped or star-shaped (co)polymers of virtually any type or geometry. One example of such an initiator is a 2,2-bis(halomethyl)-1,3-dihalopropane (e.g. 2,2-bis(chloromethyl)-1,3-dichloropropane or 2,2-bis(bromomethyl)-1,3-dibromopropane), and a preferred example is where one of R_{35} , R_{36} and R_{37} is phenyl substituted with from 1 to 5 C_{1-7} alkyl substituents, each of which may independently be further substituted with a group X_1 , e.g. α, α' -dibromoxylene, hexakis(α -chloro- or α -bromomethyl)benzene.

Preferred initiators include 1-phenylethyl chloride and 1-phenylethyl bromide, chloroform, carbon tetrachloride, 2-chloropropionitrile and C_{1-7} alkyl esters of a 2-halo- C_{1-7} saturated monocarboxylic acid (such as 2-chloropropionic acid, 2-bromopropionic acid, 2-chloroisobutyric acid, 2-bromoisobutyric acid and the like). Another example of a suitable initiator is dimethyl-2-chloro-2,4,4-trimethylglutarate.

Any transition metal complex which can participate in a redox cycle with the initiator and dormant polymer chain, but which does not form a direct carbon-metal bond with the polymer chain, such as a complex of ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, rhodium, vanadium, zinc, gold, silver, nickel or cobalt, is suitable for use in this embodiment of the invention. The amounts and relative molar proportions of the initiator and the transition metal complex of the invention are those which are typically effective to conduct ATRP. The molar proportion of the transition metal complex with respect to the initiator may be from 0.0001:1 to 10:1, preferably from 0.1:1 to 5:1, more preferably from 0.3:1 to 2:1, and most preferably from 0.9:1 to 1.1:1.

ATRP according to the invention may be conducted in the absence of a solvent, i.e. in bulk. However, when a solvent is used, suitable solvents include ethers, cyclic ethers, alkanes, cycloalkanes, aromatic hydrocarbons, halogenated hydrocarbons, acetonitrile, dimethylformamide and mixtures thereof, and supercritical solvents (such as CO₂). ATRP may also be conducted in accordance with known suspension, emulsion or precipitation methods. Suitable ethers include diethyl ether, ethyl propyl ether, dipropyl ether, methyl t-butyl ether, di-t-butyl ether, glyme (dimethoxyethane) diglyme (diethylene glycol dimethyl ether), etc. Suitable cyclic ethers include tetrahydrofuran and dioxane. Suitable alkanes include pentane, hexane, cyclohexane, octane and dodecane. Suitable aromatic hydrocarbons include benzene, toluene, o-xylene, m-xylene, p-xylene and cumene. Suitable halogenated hydrocarbons include dichloromethane, 1,2-dichloroethane and benzene substituted with 1 to 6 fluorine and/or chlorine atoms, although one should ensure that the selected halogenated hydrocarbon does not act as an initiator under the reaction conditions.

ATRP may also be conducted in the gas phase (e.g. by passing the gaseous monomer(s) over a bed of the catalytic system), in a sealed vessel or in an autoclave. (Co)polymerization may be conducted at a temperature from about 0°C to 160°C, preferably from about 60°C to 120°C. Typically, the average reaction time will be from about 30 minutes to 48 hours, more preferably from 1 to 24 hours. (Co)polymerization may be conducted at a pressure from about 0.1 to 100 atmospheres, preferably from 1 to 10 atmospheres.

According to another embodiment, ATRP may also be conducted in emulsion or suspension in a suspending medium for suspending the monomer(s) and while using the metal complex of the invention in combination with a surfactant, so as to form a (co)polymer emulsion or suspension. The suspending medium usually is an inorganic liquid, preferably water. When water or an aqueous mixture is selected as the suspending medium, it is preferable to use a cationic metal complex species as the catalytic component, the said cationic species being associated with an anion A as described hereinabove. In this embodiment of the invention, the weight ratio of the organic phase to the suspending medium is usually between 1:100 and 100:1, preferably between 1:10 and 10:1. If desired, the suspending medium may be buffered. Preferably the surfactant will be selected in order to control the stability of the emulsion, i.e. to form a stable emulsion.

In order to conduct polymerization in a heterogeneous medium (where the monomer/polymer is insoluble, or only slightly soluble, in the suspension medium, i.e. water or CO₂), the metal catalytic component should be at least partially soluble in the monomer/polymer. Thus, only when ligands

are properly selected to allow the catalyst to meet this requirement, such as ligands containing long alkyl chains to increase catalyst solubility in hydrophobic monomers targeted for polymerization, is a successful, controlled ATRP polymerization obtained in the water-borne systems of this embodiment. From the above description of ligands coordinating the metal in the catalytically active metal complexes of the invention, those skilled in the art will be able to make a suitable selection.

A key component in the preparation of the stable emulsions of the present embodiment is the use of the surfactant to stabilize the initial monomer suspension/emulsion and growing polymer particles and to prevent unwanted coagulation/flocculation of the particles. In order to conduct ATRP in emulsion however, care should be taken to choose a surfactant which does not interfere with the catalytic component or dormant chain end. Suitable surfactants for this purpose include non-ionic, anionic, and cationic surfactants, with cationic and non-ionic surfactants being preferred in non-buffered solutions. Particularly preferred non-ionic surfactants include polyethylene glycol, polyoxyethylene oleyl ethers and polyoxyethylene sorbitan monoalkyls. A preferred cationic surfactant is dodecyltrimethyl ammonium bromide. Regardless of the surfactant used, efficient stirring is preferred to obtain good dispersions or latexes.

The surfactant is usually present in a concentration of about 0.01% to 50% by weight based on the total weight of all components introduced into the polymerisation reactor, i.e. suspending medium, monomer(s), surfactant and catalytic system.

High solubility in the suspension medium is not a prerequisite for the initiator as may be demonstrated by the use of the poorly water soluble ethyl 2-bromoisobutyrate, to initiate emulsion polymerization. While any order of addition of the initiator and other reaction components can be used, however if the initiator is added to a pre-emulsified reaction mixture, stable latexes are usually obtained. Suitable initiators have been described herein-above in the solvent embodiment of the ATRP process. Initiators can also be macromolecules that contain radically transferable atoms or groups. A special type of such macroinitiators may be water-soluble or even amphiphilic and may, after initiation of the reaction, be incorporated into the polymer particle and may stabilize the growing particle due to the hydrophilic segment of the macroinitiator.

After completing the (co)polymerization step of the ATRP process of this invention, the polymer formed may be isolated by known procedures, such as, but not limited to, precipitating in a suitable solvent, filtering the precipitated polymer, then washing and drying the filtered polymer. Precipitation can be typically conducted using a suitable alkane or cycloalkane solvent, such as pentane hexane, heptane, cyclohexane or mineral spirits, or using an alcohol, such as methanol, ethanol or isopropanol, or any mixture of suitable solvents. The precipitated (co)polymer can be filtered by gravity or by vacuum filtration, e.g. using a Buchner funnel and an aspirator. The polymer can then be washed with the solvent used to precipitate the polymer, if desired. The steps of precipitating, filtering and washing may be repeated, as desired. Once isolated, the (co)polymer may be dried by drawing air through the (co)polymer, by vacuum. The dried (co)polymer can then be analyzed and/or characterized e.g. by size exclusion chromatography or NMR spectroscopy.

(Co)polymers produced by the catalytic ATRP process of the invention may be useful in general as molding materials (e.g. polystyrene) and as barrier or surface materials (e.g. polymethyl

methacrylate). However, since they typically have more uniform properties (in particular molecular weight distribution) than polymers produced by conventional radical polymerization, they will be most suitable for use for specialized applications. For example, block copolymers of polystyrene (PSt) and polyacrylate (PA), e.g. PSt-PA-PSt triblock copolymers, are useful thermoplastic elastomers. Polymethylmethacrylate/acrylate triblock copolymers (e.g. PMMA-PA-PMMA) are useful, fully acrylic, thermoplastic elastomers. Homo- and copolymers of styrene, (meth)acrylates and/or acrylonitrile are useful plastics, elastomers and adhesives. Either block or random copolymers of styrene and a (meth)acrylate or acrylonitrile are useful thermoplastic elastomers having high solvent resistance. Furthermore, block copolymers in which blocks alternate between polar monomers and non-polar monomers produced by the present invention are useful amphiphilic surfactants or dispersants for making highly uniform polymer blends. Star-shaped (co)polymers, e.g. styrene-butadiene star block copolymers, are useful as having high impact resistance.

(Co)polymers produced by the catalytic ATRP process of the present invention typically have a number average molecular weight from about 5,000 to 1,000,000, preferably from about 10,000 to 250,000, and more preferably from about 25,000 to 150,000.

Because ATRP is a living polymerization process, it can be started and stopped practically at will. Further, the polymer product retains the functional group X_1 necessary to initiate a further polymerization. Thus, in a specific embodiment, once a first monomer is consumed in the initial polymerizing step, a second monomer can then be added to form a second block on the growing polymer chain in a second polymerizing step. Further additional polymerizations with the same or different monomer(s) can be performed to prepare multi-block copolymers. Furthermore, since ATRP is also a radical polymerization, these blocks can be prepared in essentially any order.

(Co)polymers produced by the catalytic ATRP process of the present invention have a very low polydispersity index, i.e. the ratio M_w/M_n of their weight average molecular weight to their number average molecular weight is typically from about 1.1 to 2.4, preferably from 1.15 to 2.0, more preferably from 1.2 to 1.6.

Because the living (co)polymer chains retain an initiator fragment including X_1 as a terminal group, or in one embodiment as a substituent in a monomeric unit of the polymer chain, they may be considered as end-functional or in-chain functional (co)polymers. Such (co)polymers may thus be converted into (co)polymers having other functional groups (e.g. halogen can be converted into hydroxy or amino by known methods, and nitrile or carboxylic ester can be hydrolyzed to a carboxylic acid by known methods) for further reactions, including crosslinking, chain extension with reactive monomers (e.g. to form long-chain polyamides, polyurethanes and/or polyesters), reactive injection molding, and the like.

In order to facilitate the use of metal complexes of the invention in the above-mentioned heterogeneous catalytic reactions, the present invention further provides silyl derivatives of such complexes, being suitable for covalent bonding to a carrier, especially those complexes wherein the multidentate ligand is a bidentate or tridentate Schiff base, e.g. one having the general formula (IA) or (IB) referred to in figure 1, or a tetradentate ligand comprising two Schiff bases such as one

having the general formula (IIA) or (IIB) or (IIC) referred to in figure 2 or the general formula (IIIA) or (IIIB) referred to in figure 3. In such silyl derivatives, R' and/or R" of the said general formula is replaced or substituted with a group having the formula:



- 5 - R₂₀ is a radical selected from the group consisting of C₁₋₇ alkylene, arylene, heteroarylene and C₃₋₁₀ cycloalkylene, the said radical being optionally substituted with one or more R₂₄ substituents each independently selected from the group consisting of C₁₋₂₀ alkyl, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, C₂₋₂₀ alkoxycarbonyl, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkynylsulfinyl, C₁₋₂₀ alkylthio, aryloxy and aryl;
- 10 - D is a divalent atom or radical selected from the group consisting of oxygen, sulphur, silicon, arylene, methylene, CHR₂₄, C(R₂₄)₂, NH, NR₂₄ and PR₂₄;
- R₂₁, R₂₂ and R₂₃ are each independently selected from the group consisting of hydrogen, halogen and R₂₄; and
- n is an integer from 1 to 20;
- 15 provided that at least one of R₂₁, R₂₂ and R₂₃ is selected from the group consisting of C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, C₂₋₂₀ alkoxycarbonyl, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkynylsulfinyl, C₁₋₂₀ alkylthio and aryloxy.

More preferred within the above group are silyl derivatives wherein R' is replaced or substituted with a 3-(triethoxysilyl)propyl or 2-(triethoxysilyl)ethyl group. Alternatively suitable derivatives include shaped organosiloxane copolycondensation products such as disclosed in EP-A-484,755.

In another embodiment, the invention provides a supported catalyst, especially for use in the above-mentioned catalytic reactions, comprising the product of covalent bonding of (a) a silyl derivative of a metal complex such as defined hereinabove, and (b) a carrier including one or more inorganic oxides or an organic polymeric material. Preferably the said inorganic carrier is selected from silica, alumino-silica, zirconia, natural and synthetic zeolites and mixtures thereof, or the said organic polymeric carrier is a polystyrene resin or a derivative thereof wherein the aromatic ring is substituted with one or more groups selected from C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl. More detailed examples of suitable carriers (b) for this purpose were already disclosed with respect to the fifth aspect of the invention.

The catalytic component of the sixth aspect of this invention is also useful in the cyclopropanation of ethylenically unsaturated compounds, or the intramolecular cyclopropanation of α -diazoketones or α -diazo- β -ketoesters for producing compounds having one or more cyclopropane structural units in the hydrocarbon chain. This embodiment of the invention is thus useful in one or more manufacturing steps of the following natural and synthetic cyclopropyl-containing compounds. Cyclopropyl-containing compounds may be found in naturally occurring terpenes, steroids, amino-acids, fatty acids, alkaloids and nucleic acids. For instance, chrysanthemic acid derivatives (such as pyrethrines) produced in plants are precursors to potent insecticides. The invention is also applicable to making synthetic pyrethroid insecticides such as deltamethrin, as well as sirenine, aristolon, sesquicarene and cyclopropyl derivatives being

intermediates in the synthesis of the steroid hirsutene or the antibiotic sarkomycine. Cyclopropyl-containing non-natural compounds also have biological activity, such as Cipro, a powerful anti-anthrax drug, or cyclopropane amino-acids (e.g. 2,3-methanophenylalanine, the anti-Parkinson drug 2,3-methano-*m*-tyrosine, coronatine and coronamic acid). Polycyclopropane fatty acid derivatives isolated from fungi, U-106305 (a cholesteryl ester transfer protein inhibitor) and FR-900848 (a nucleoside analogue), are also candidates for such synthetic production. Ethylenically unsaturated compounds that may be cyclopropanated according to this invention into the correspondingly cyclopropyl-containing compounds are not particularly limited but include, without restriction, compounds having terminal ethylenic unsaturation such as styrene (which, in the presence of ethyl diazoacetate, may be transformed into ethyl-2-phenylcyclopropanecarboxylate) and substituted derivatives thereof (e.g. 4-chlorostyrene, α -methylstyrene and vinylstyrene), 2-vinylnaphthalene, 1,1-diphenylethylene, 1-decene, functional α -olefins wherein the functional group is preferably adjacent to the ethylenic unsaturation and is preferably a protected alcohol such as in protected allylic alcohols such as acyclic allylic silyl ethers (which may be transformed into cyclopropylcarbiny silyl ethers) or a carboxy group such as in acrylic and methacrylic acids (as well as esters, thioesters, amides or anhydrides thereof), cinnamate esters, alkenylboronic esters (such as 2-methylethenyl-4,5-bis[methoxy-diphenylmethyl]-1,3,2-dioxaborolanes or derivatives thereof wherein the methyl group is protected by a protecting group such as, but not limited to, *tert*-butyldimethylsiloxy, *tert*-butyldiphenylsiloxy, benzyloxy, methoxymethoxy or benzoyloxy, which may be transformed into the corresponding cyclopropylboronic esters), 2-phenylsulfonyl-1,3-dienes and cycloolefins such as cyclooctene. Such reaction preferably takes place in the presence of a diazo compound such as, but not limited to, ethyl diazoacetate, cinnamyl diazoacetate, dicyclohexylmethyl diazoacetate, vinyl diazoacetate, menthyl diazoacetate or 1-diazo-6-methyl-5-hepten-2-one, at moderate temperatures usually ranging from about 0°C to 80°C, preferably 20 to 60°C, the reaction time ranging from about 1 to 12 hours, and in a relatively low boiling solvent such as methylene chloride, tetrahydrofuran, ethanol, isopropanol, *tert*-butanol, L-menthol or water, or mixtures thereof. The diazo compound may be added as such or, in order to eliminate the handling risks associated with its explosive nature, may be generated *in situ* by reacting an acetoammonium salt with sodium nitrite in the presence of the ethylenically unsaturated compound. When water or an aqueous mixture is selected as the reaction solvent, it is preferable to use a cationic metal complex species as the catalytic component, the said cationic species being associated with an anion A as described hereinabove. Preferably the molar ratio of the ethylenically unsaturated compound to the catalytic component is in a range from 200 to 2,000, more preferably from 250 to 1,500. The molar ratio of the ethylenically unsaturated compound with respect to the diazo compound is conventional for this kind of reaction, i.e. a molar excess of the former compound. The cyclopropanation of ethylenically unsaturated compounds may optionally be carried out in the presence of a tertiary aliphatic amine, such as triethylamine or tri-*n*-butylamine, or a heterocyclic amine such as pyridine or lutidine as a co-catalyst. The intramolecular cyclopropanation of α -diazo carbonyl compounds such as α -diazo ketones or α -diazo- β -ketoesters may also be performed according to similar reaction conditions (temperature, reaction time,

substrate/ catalyst ratio) and may result in bicyclic molecules wherein the cyclopropyl group may be fused to another cycloaliphatic group, e.g. a cyclopentanone such as in the synthesis of intermediates of hirsutene or sarkomycin, or a cyclopentyl group when starting from acetylenic α -dialkyl ketones. However, it should be noted that, in accordance with the teachings of Padwa in *Molecules* (2001) 6:1-12, the cyclisation of an acetylenic α -dialkyl ketone in the presence of a catalytic component of this invention may also lead to the formation of other polycyclic ring systems such as, but not limited to, cyclopentanone fused to a furan, an alkenyl-substituted indenone, a cyclopropyl-substituted indenone, a cyclopentazulenone or a cyclopentadiene fused to indenone.

The catalytic component of the sixth aspect of this invention is also useful in the cyclopropenation of alkynes for producing compounds having one or more cyclopropene structural units in the hydrocarbon chain. This applies in particular to alkynes having a C_{2-7} alkynyl group such as, but not limited to, 1-hexyne, 3,3-dimethyl-1-butyne, phenylacetylene, cyclohexylacetylene, methoxy-methylacetylene and acetoxymethylacetylene which may be converted in good yields into ethylcyclopropene-3-carboxylates in the presence of a diazo compound such as, but not limited to, ethyl diazoacetate, cinnamyl diazoacetate, dicyclohexylmethyl diazoacetate, vinyl diazoacetate, 1-diazo-6-methyl-5-hepten-2-one or menthyl diazoacetate. It is also useful in the intramolecular cyclopropenation of acetylenic α -dialkyl ketones, leading for instance to cyclopropenyl-containing compounds such as cyclopropenyl substituted indenones.

The catalytic component of the sixth aspect of this invention is also useful in quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones (i.e. the so-called Friedlaender reaction). Such reaction preferably takes place with a molar excess of the said ketone, under basic conditions (such as in the presence of an alkali hydroxide), at moderate temperatures usually ranging from about 20 to about 100°C and optionally in the presence of a solvent. Preferably the ratio of the 2-aminobenzyl alcohol to the catalytic component is in a range from 100 to 2,000, preferably from 200 to about 1,000. A number of alkylarylketones, alkyl heteroarylketones, dialkylketones and benzo-fused cyclic ketones may be used in this process of the invention, including C_{1-7} alkylketones wherein the second hydrocarbon attached to the oxo group may be methyl, pentyl, isopropyl, phenethyl, phenyl, toluyl, anisyl, nitrophenyl, hydroxyphenyl, fluorophenyl, trifluoromethylphenyl, cyanophenyl, naphthyl, furanyl, thiophenyl, pyridyl, and the like. Exemplary ketones which may be cyclised to quinolines according to this embodiment of the invention include, but are not limited to, acetophenone, 3-methylacetophenone, cyclohexanone, 4-phenylcyclohexanone and propiophenone. Other suitable ketones for this purpose are as disclosed by Cho et al. in *Chem. Commun.* (2001) 2576-2577. Unexpectedly, some ketones such as cyclohexanone may be converted into the corresponding quinoline with a yield significantly higher, under equivalent reaction conditions, than achieved by the ruthenium catalyst used in the latter publication.

The catalytic component of the sixth aspect of this invention is also useful in the intramolecular epoxidation, including the asymmetric epoxidation, of ethylenically unsaturated compounds, i.e. alkenes, for producing the corresponding epoxides (i.e. oxacyclopropyl-containing compounds). Such alkenes include for instance, but without limitation, styrene and analogues thereof (such as α -

methylstyrene, p-chlorostyrene, p-trifluoromethylstyrene and the like) or cholesterol acetate. Illustrative olefinic starting reactants useful in the asymmetric epoxidation of this invention include those which can be terminally or internally unsaturated and be of straight chain, branched chain, or cyclic structure. Such olefinic reactants may contain from 3 to about 40 carbon atoms and may contain one or more ethylenically unsaturated groups. Moreover, such olefinic reactants may contain groups or substituents which do not essentially adversely interfere with the asymmetric epoxidation process such as carbonyl, carbonyloxy, oxy, hydroxy, oxycarbonyl, halogen, alkoxy, aryl, haloalkyl, and the like. Illustrative olefinic unsaturated compounds include substituted and unsubstituted alpha-olefins, internal olefins, alkyl alkenoates, alkenyl alkanoates, alkenyl alkyl ethers, alkenols, and the like, e.g. propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-octadecene, 2-butene, isoamylene, 2-pentene, 2-hexene, 3-hexene, 2-heptene, cyclohexene, 2-ethylhexene, 3-phenyl-1-propene, 1,4-hexadiene, 1,7-octadiene, 1,5,9-dodecatriene, 3-cyclohexyl-1-butene, allyl alcohol, hex-1-en-4-ol, oct-1-en-4-ol, vinyl acetate, allyl acetate, aryloates such as vinyl benzoate and the like, 3-butenyl acetate, vinyl propionate, allyl propionate, allyl butyrate, methyl methacrylate, 3-butenyl acetate, vinyl ethyl ether, vinyl methyl ether, allyl ethyl ether, n-propyl-7-octenoate, substituted and unsubstituted chromenes, 2,2-dimethylcyclochromene, 3-butenenitrile, 5-hexenamide, indene, 1,2-dihydronaphthalene, 2-vinylnaphthalene, norbornene, cis-stilbene, trans-stilbene, p-isobutylstyrene, 2-vinyl-6-methoxynaphthylene, 3-ethenylphenyl phenylketone, 4-ethylphenyl-2-thienylketone, 4-ethenyl-2-fluorobiphenyl, 4-(1m,3-dihydro-1-oxo-2H-isoindol-2-yl) styrene, 2-ethyl-5-benzoylthiophene, 3-ethenylphenyl phenylether, isobutyl-4-propenylbenzene, phenyl vinyl ether, 2-cyclohexenyl-1,1-dioxolane, vinyl chloride, benzopyrane and benzofurane type compounds, and substituted aryl ethylenes such as described in U.S. Pat. No. 4,329,507, incorporated herein by reference in its entirety. Epoxidation of the invention may be applied to the synthesis of biologically active molecules such as cis-stilbene oxide (a substrate for microsomal and cytosolic epoxide hydrolase) and isoprostane.

Such epoxidation reaction preferably takes place in the presence of an at least stoichiometric amount (with respect to the ethylenically unsaturated compound) of an oxygen atom source or oxygen-transfer reagent being relatively unreactive toward olefins in the absence of the catalytic system. The said oxygen atom source or oxygen-transfer reagent may be, but without limitation, selected from the group consisting of NaOCl, iodosylmesitylene, NaIO₄, NBu₄IO₄, potassium peroxymonosulfate, magnesium monoperoxyphthalate, 2,6-dichloropyridine N-oxide and hexacyanoferrate ion. Such epoxidation reaction preferably takes place under conditions and for such time as is needed to epoxidize the olefinic unsaturated compound. Such conditions include, but without limitation:

- reaction temperatures usually ranging from about -20° C to about 120° C, preferably from 0° C to 90° C, more preferably from 20 to about 40°C, and/or
- reaction pressures ranging from about 0.1 to about 70 bars, and/or
- conducting the reaction in the presence of a solvent for the catalytic system, preferably a relatively low boiling organic solvent selected from the group consisting of saturated alcohols, amines, alkanes, ethers, esters, aromatics and the like, and/or

- a molar ratio of the ethylenically unsaturated compound to the catalytic component in a range from about 200 to about 20,000, preferably from 500 to 10,000, and/or
- a molar excess of the oxygen-transfer reagent with respect to the olefinic unsaturated compound.

5 The catalytic component of the sixth aspect of this invention is also useful in the oxidation of hydrocarbons into alcohols such as, but not limited to, the oxidation of methane (which is known to be more difficult to oxidize than other alkanes) into methanol. Although this process is effective for a wide variety of hydrocarbons, it is particularly effective for the oxidation of straight chain and branched chain alkanes and cycloalkanes with 1 to 15 carbon atoms, and arylalkanes such as
10 toluene, xylene and ethylbenzene. The preferred aliphatic hydrocarbons have 1 to 10 carbon atoms, including ethane, propane, butane, isobutane, hexanes, and heptanes; and the preferred cyclic hydrocarbons have 5 to 10 carbon atoms such as cyclopentane, cyclohexane, cycloheptane, cyclooctane and adamantane. This invention is also applicable to a broad range of hydrocarbons containing various substituents to enhance the rate of oxidation. Oxidation according to this
15 invention may be carried out in a liquid phase, mixed solvent system such as water/acetone, water/acetonitrile and/or acetic acid, which is inert to the conditions of the reaction and to oxidation by molecular oxygen. The temperature can range between 20 and 60 °C. The pressure may range from 5 to 20 atmospheres. Depending upon whether the hydrocarbon is a solid, liquid or gas, it is either dissolved in the mixed solvent system or is bubbled through the solvent together with air or
20 oxygen before adding the catalytic component of the invention. A concentration ranging from 10^{-3} to 10^{-6} moles of the catalytic component in solution is usually sufficient to achieve the desired oxidation. The reaction time preferably ranges from 30 minutes to 30 hours, more preferably from 1 to 5 hours. According to another embodiment, the catalytic component of the sixth aspect of this invention is also useful in the oxidation of allylic and benzylic alcohols into carbonyl compounds.

25 The sixth aspect of the present invention also relates to other atom or group transfer reactions such as asymmetric syntheses in which a prochiral or chiral compound is reacted in the presence of an optically active, metal-ligand complex catalyst, in enantiomerically active form, to produce an optically active compound. These reactions, which are useful for the production of numerous classes of products, e.g. sulfoxides, aziridines, enol esters, nitriles, silanes, silyl ethers, alkanes,
30 phosphonates, alkylboranes, hydroxycarbonyl compounds, β -cyano carbonyl compounds, carboxyl compounds, arylalkenes, heteroarylalkenes, cyclohexenes, 7-oxanorbornenes, aldehydes, alcohols, primary or secondary amines, amides and the like, have been listed hereinbefore and will be detailed below.

For instance, the catalytic oxidation of sulfides (into sulfoxides and sulfones), phosphines (into
35 phosphonates), and alcohols or aldehydes into carboxylic acids can be carried out in accordance with conventional oxidation procedures known in the art. For example, but without limitation, optically active carboxylic acids can be prepared by reacting a racemic aldehyde and an oxygen atom source in the presence of an optically active metal complex catalytic system as described herein. A number of sulfoxides finding application in the pharmaceutical industry, such as a
40 quinolone sulfoxide described by Matsugi et al. in *Tetrahedron* (2001) 57:2739 (a platelet adhesion

inhibitor), or a pyrazolotriazine sulfoxide described by Naito et al. in *Yakugaku Zasshi* (2001) 121:989 (a drug for the treatment of hyperurecemia and ischemic reperfusion injury), or methylphenyl sulfoxide (from methylphenyl thioether) may be made by using such a process step.

Catalytic hydrocyanation (or cyanohydration) of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for producing β -cyano carbonyl compounds can be carried out in accordance with conventional procedures known in the art. For example, 1-phenyl propenone may be transformed into 4-oxo-4-phenyl-butanenitrile, or optically active nitrile compounds can be prepared by reacting a prochiral olefin and hydrogen cyanide in the presence of an optically active metal complex catalytic system as described herein.

Catalytic hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trialkylsilyl-cyanation of aldehydes (e.g. benzaldehyde) for producing cyanohydrin trialkylsilyl ethers (which may afterwards be hydrolysed into cyanohydrins) can be carried out in accordance with conventional procedures known in the art. For example, optically active silanes or silyl ethers can be prepared by reacting a prochiral olefin or ketone or aldehyde together with a suitable silyl compound under conventional hydrosilylation conditions in the presence of an optically active metal complex catalytic system described herein. Hydrosilylation of olefins, in which a silane reactant R_3SiH is added to an unsaturated carbon-carbon bond in the presence of a catalyst, as well as hydrosilylation of carbonyl compounds, including aldehydes, ketones and thioketones, is extensively reported by Ojima et al. in "The Chemistry of Organic Silicon Compounds", vol. 2 (New York, Wiley and Sons, 1998), pages 1687-1792.

Catalytic aziridination of imines or alkenes for producing organic compounds having one or more aziridine structural units can be carried out in accordance with conventional procedures known in the art. For example, prochiral olefins can be converted to optically active aziridines under conventional aziridination conditions in the presence of an optically active metal complex catalytic system as described herein.

Catalytic hydroamidation of olefins for producing saturated amides can be carried out in accordance with conventional procedures known in the art. For example, optically active amides can be prepared by reacting a prochiral olefin, carbon monoxide, and a primary or secondary amine or ammonia under conventional hydroamidation conditions in the presence of an optically active metal complex catalytic system as described herein.

Catalytic hydrogenation of olefins into alkanes, or ketones into alcohols can be carried out in accordance with conventional procedures known in the art. For example, a ketone can be converted to an optically active alcohol under conventional hydrogenation conditions in the presence of an optically active metal complex catalytic system as described herein. Substrates that can be hydrogenated in accordance with this embodiment of the invention include, but are not limited to, α -(acylamino) acrylic acids (thus enantioselectively providing chiral amino-acids), α -acetamidocinnamic acid, α -benzamidocinnamic acid, dehydroamino acid derivatives and methyl esters thereof, imines, β -ketoesters (such as methyl acetylacetate) and ketones.

Catalytic aminolysis or hydroamination of olefins for producing saturated primary or secondary amines can be carried out in accordance with conventional procedures known in the art. For example, optically active amines can be prepared by reacting a prochiral olefin with a primary or secondary amine under conventional aminolysis conditions in the presence of an optically active metal complex catalytic system as described herein. The hydroamination reaction may involve a silylazide, e.g., a trialkylsilylazide, and an unsaturated reactant in the form of an alkene or alkyne, i.e. the reaction may proceed first through the formation of a β -azidoalkylsilane which can then undergo desilylation and reduction of the azide to an amine. Reaction of an alkyne with a trialkylsilylazide produces a vinyl silane that can be further employed in a cross-coupling reaction, in which reduction of the azide intermediate is followed by hydrolysis of the resultant imine to give a ketone, effectively performing a regioselective hydration of a disubstituted alkyne.

The present invention is also useful in the silylmetalation of unsaturated compounds, particularly olefins and carbonyl compounds. The adducts formed upon silylmetalation are useful as intermediates in the further synthesis of a variety of compounds. For example, silylboration of a ketone produces a silyl ether containing a quaternary carbon-boron bond, and subsequent Suzuki cross coupling allows for the introduction of a variety of aryl, vinyl and alkyl halides.

The catalytic species of this invention are also applicable to carbometalation reactions such as, but not limited to, the addition of silyl cyanides and allyl silanes to carbonyl compounds and other types of unsaturated substrates. For example, the catalyzed reaction of trimethylsilyl cyanide with an olefin, followed by protodesilylation, produces the equivalent of a Markovnikov hydrocyanation reaction. Transition metal catalyzed cross-coupling using the catalysts and methods of the invention thus provides a stereoselective synthetic route to trisubstituted olefins. Similar reactions can be conducted with allyl silanes in which the activation of the silicon-carbon bond produces a siloxymetal allyl intermediate that can further react with a variety of functional groups (for example, the reaction of an allyl silane with an olefin, followed by protodesilylation).

The catalytic species of this invention are also applicable to Suzuki-Miyaura cross-coupling reactions such as, but not limited to, the coupling of an aryl bromide (e.g. 4-bromotoluene) with an arylboronic acid (e.g. phenylboronic acid).

Catalytic isomerization of alcohols, preferably allylic alcohols, for producing aldehydes can be carried out in accordance with conventional procedures known in the art. For example, allylic alcohols can be isomerized under conventional isomerization conditions to produce optically active aldehydes in the presence of an optically active metal complex catalytic system described herein.

Catalytic Grignard cross coupling of alkyl or aryl halides for producing alkanes or arylalkanes can be carried out in accordance with conventional procedures known in the art. For example, optically active alkanes or arylalkanes can be prepared by reacting a chiral Grignard reagent with an alkyl or aryl halide under conventional Grignard cross coupling conditions in the presence of an optically active metal complex catalytic system as described herein.

Catalytic hydroboration of olefins (such as, but not limited to, 4-methyl-1-pentene) for producing alkylboranes and trialkylboranes (which may then be oxidised or hydrolysed into alcohols) can be carried out in accordance with conventional procedures known in the art. For example, optically

active alkyl boranes or alcohols can be prepared by reacting a prochiral olefin and a borane under conventional hydroboration conditions in the presence of an optically active metal complex catalytic system as described herein.

5 Catalytic hydride reduction of aldehydes and ketones for producing alcohols can be carried out in accordance with conventional procedures known in the art, i.e. by treating the said aldehyde or ketone with a hydride reagent such as sodium borohydride or alithium aluminum hydride. For example, pentanal may be reduced into 1-pentanol, cyclobutanone into cyclobutanol, and cyclohexane-1,4-dione into 1,4-cyclohexanediol.

10 Catalytic aldol condensation of saturated carboxyl compounds (aldehydes or ketones) for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intramolecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds (aldehydes or ketones) can be carried out in accordance with conventional procedures known in the art. For example, optically active aldols can be prepared by reacting a prochiral ketone or aldehyde and a protected enol such as a silyl enol ether under conventional
15 aldol condensation conditions in the presence of an optically active metal complex catalytic system as described herein.

Catalytic codimerization of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes can be carried out in accordance with conventional procedures known in the art. For example, optically active hydrocarbons can be prepared by reacting a prochiral alkene
20 and another alkene under codimerization conditions in the presence of an optically active metal complex catalytic system as described herein.

Catalytic alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones, can be carried out in accordance with conventional procedures known in the art in the presence of a metal complex catalytic system as described herein. Similarly, 1,3-diphenyl-2-propenyl acetate may be alkylated with a nucleophile such as $\text{CH}_2(\text{CO}_2\text{CH}_3)_2$ in the
25 presence of the catalytic component of the invention.

Catalytic Diels-Alder reactions such as, but not limited to, the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for
30 producing optionally substituted 7-oxanorbornenes can be carried out in accordance with conventional procedures known in the art in the presence of a metal complex catalytic system as described herein.

Catalytic Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds can be carried out in
35 accordance with conventional procedures known in the art in the presence of a metal complex catalytic system as described herein, i.e. for example an enolate ion may undergo conjugate addition to an α,β -unsaturated aldehyde or ketone, such as for example the addition of acrolein onto 2,4-pentanedione (acetylacetone) or 2-methylcyclohexanone. With some Michael acceptors, such as 3-buten-2-one, the products of the initial addition are capable of a subsequent

intramolecular aldol condensation, the so-called Robinson annulation, e.g. the addition of 3-buten-2-one onto 2-methylcyclohexanone.

Catalytic Heck reactions can be carried out in accordance with conventional procedures known in the art in the presence of a metal complex catalytic system as described herein. The standard
5 Heck reaction, especially with the metal of the catalytic component being palladium, involves the reaction of an aryl or heteroaryl halide, e.g. 3-bromoquinoline, with an alkene, commonly an acrylate. An oxidative variant of the Heck reaction proceeds from certain heterocyclic compounds such as indoles, furans and thiophenes such as, but not limited to, N-acetyl-3-methylindole. A reductive variant of the Heck reaction proceeds from certain 3-acylpyridines, 4-acylpyridines and
10 acylindoles, e.g. the reaction of 3-acetylpyridine with triethoxysilylethylene.

The permissible prochiral and chiral starting material reactants encompassed by the processes of this invention are, of course, chosen depending on the particular synthesis and product desired. Such starting materials are well known in the art and can be used in conventional amounts in accordance with conventional methods. Illustrative starting material reactants include, for example,
15 aldehydes (e.g. for intramolecular hydroacylation, aldol condensation, and oxidation into acids), prochiral olefins (e.g. for epoxidation, hydrocyanation, hydrosilylation, aziridination, hydroamidation, aminolysis, cyclopropanation, hydroboration, Diels-Alder reaction and codimerization), ketones (e.g. for hydrogenation, hydrosilylation, aldol condensation, Robinson annulation, transfer hydrogenation and allylic alkylation), alkynes (e.g. for cyclopropanation), epoxides (e.g. for
20 hydrocyanation or nucleophilic ring opening reaction), alcohols (e.g. for carbonylation), aryl halides (e.g. for decarbonylation and Heck reactions), and chiral Grignard reagents (e.g. for Grignard cross coupling).

In one embodiment of the sixth aspect of the invention, the multidentate ligand and the other ligands, in particular L^5 and L^6 , are defined as for the main catalytic species of the catalytic system
25 of the fourth aspect of the invention. Preferably, the multidentate ligand of the metal complex used as a catalytic component is a bidentate or tridentate Schiff base such as defined hereinabove and more specifically as illustrated in figure 1.

In another embodiment of the sixth aspect of the invention, the catalytic component may also be a five-coordinate metal complex, a salt, a solvate or an enantiomer thereof, comprising a carbene
30 ligand, a multidentate ligand and one or more other ligands, wherein at least one of said other ligands is a constraint steric hindrance ligand having a pKa of at least 15, this kind of metal complex being already described in International Patent Application published as WO 03/062253, the content of which is incorporated herein by reference. Within this embodiment, it is especially preferred when:

- 35
- the metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table, more preferably the metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt; and/or

- the multidentate ligand is a bidentate ligand and the metal complex comprises two other ligands, or the multidentate ligand is a tridentate ligand and the metal complex comprises a single other ligand; and/or
- the carbene ligand is a benzyldiene, vinylidene, indenylidene or allenylidene ligand or a cumulenylidene ligand, e.g. buta-1,2,3-trienylidene or penta-1,2,3,4-tetra-enylidene; and/or
- one of said other ligands is an anionic ligand, or one of said other ligands is a solvent (which may be selected from the group consisting of protic solvents, polar aprotic solvents and non-polar solvents, including aromatic hydrocarbons, chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, esters, ketones, amides and water) and the complex is a cationic species associated with an anion (which may be selected from the group consisting of hexafluorophosphate, hexafluoroantimoniate, hexafluoroarsenate, tetrafluoroborate, tetra(pentafluorophenyl)borate, perchlorate, alkylsulfonates wherein the alkyl group may be substituted with one or more halogen atoms such as trifluoromethanesulfonate, and arylsulfonates); and/or
- said constraint steric hindrance ligand having a pKa of at least 15 may be a derivative, wherein one or more hydrogen atoms is substituted with a group providing constraint steric hindrance, of a non-ionic phosphatane superbase or a N-heterocyclic carbene selected from the group consisting of imidazol-2-ylidene, dihydroimidazol-2-ylidene, oxazol-2-ylidene, triazol-5-ylidene, thiazol-2-ylidene, bis(imidazoline-2-ylidene) bis(imidazolidine-2-ylidene), pyrrolylidene, pyrazolylidene, dihydropyrrolylidene, pyrrolylidinylidene and benzo-fused derivatives thereof.

Within this embodiment, more preferably the multidentate ligand is a bidentate Schiff base having one of the general formulae (IA) or (IB) referred to in figure 1, wherein Z, R', R'' and R''', and optionally R'''' and R₅, are as defined hereinabove in a specific embodiment of the first and second aspects of the present invention.

In yet another embodiment of the sixth aspect of the invention, the catalytic component may also be a tetra-coordinated or penta-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- a tetradentate ligand comprising two Schiff bases, and
- optionally a solvent ligand (which may be selected from the group consisting of protic solvents, polar aprotic solvents and non-polar solvents, including aromatic hydrocarbons, chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, esters, ketones, amides and water), the said metal complex then being associated with an anion (which may be selected from the group consisting of hexafluorophosphate, hexafluoroantimoniate, hexafluoroarsenate, tetrafluoroborate, tetra(pentafluorophenyl)borate, perchlorate, alkylsulfonates wherein the alkyl group may be substituted with one or more halogen atoms such as trifluoromethanesulfonate, and arylsulfonates), or an anionic ligand (which may be selected from the group consisting of C₁₋₂₀ carboxylate, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyloxy, C₂₋₂₀ alkynyloxy, aryloxy, C₁₋₂₀ alkoxycarbonyl, C₁₋₈ alkylthio, C₁₋₂₀ alkylsulfonyl, C₁₋₂₀ alkylsulfinyl, C₁₋₂₀ alkylsulfonate, arylsulfonate, C₁₋₂₀ alkylphosphonate,

arylphosphonate, C₁₋₂₀ alkyl-ammonium, arylammonium, alkyldiketonate (e.g. acetylacetonate), aryldiketonate, halogen, nitro and cyano).

Tetradentate ligands comprising two Schiff bases being suitable for this embodiment include for instance, but without limitation:

- 5 - the N,N,N,O- tetradentate ligands having the general formula (IIIA) shown in figure 3, wherein R₁ and R₂ are independently selected from the group consisting of hydrogen, C₁₋₂₀ alkyl and aryl (in particular phenyl, naphthyl and anthracyl), or R₁ and R₂ together form a homocyclic or heterocyclic ring having a total of 3 to 10 atoms, wherein the said C₁₋₂₀ alkyl, aryl, homocyclic and/or heterocyclic groups may be substituted with one or more
10 substituents selected from the group consisting of nitro, halogen, C₁₋₇ alkoxy, carboxylate, amino, amido, silyl, and siloxyl; each of groups R₃ and R₁₃ is a leaving group, e.g. selected from the group consisting of hydrogen and C₁₋₂₀ alkyl; each of groups R₄, R₅, R₆ and R₇ is independently selected from the group consisting of C₁₋₇ alkyl, aryl, nitro, halogen, hydrogen, C₁₋₇ alkoxy, carboxylate, amino; amido, silyl and siloxyl, or two adjacent such
15 groups together form an optionally substituted homocyclic or heterocyclic ring having a total of 3 to 10 atoms; each of groups R₈, R₉, R₁₀, R₁₁ and R₁₂ is independently selected from the group consisting of hydrogen, C₁₋₂₀ alkyl and aryl (in particular phenyl, naphthyl and anthracyl), or R₉ and R₁₀ together form a homocyclic or heterocyclic ring having a total of 3 to 10 atoms, and/or R₁₁ and R₁₂ together form a homocyclic or heterocyclic ring having
20 a total of 3 to 10 atoms; the number n of carbon atoms between C₁ and C₂ is an integer from 0 to 2, preferably 0; and C₁ and C₂ may independently or jointly be part of an aryl group; as can easily be understood, each of groups R₃ and R₁₃ will be cleaved off when coordination with the metal occurs.
- 25 - the N,N,N,N- tetradentate ligands having the general formula (IIIB) shown in figure 3, wherein R₁ and R₂ are each independently selected from the group consisting of hydrogen and carbon-containing moieties (e.g. benzyl), most preferably having an amino-acid side chain; each of groups R₃, R₄, R₅ and R₆ is independently selected from the group consisting of organic moieties, preferably a moiety having a ring structure, more preferably a phenyl group; and G is selected from the group consisting of boron, aryl groups (e.g.
30 phenyl or naphthyl), aliphatic saturated (e.g. C₁₋₇ alkylene and C₃₋₁₀ cycloalkylene) and unsaturated (e.g. olefinic) chains; complexes formed between these ligands and a metal selected from the group consisting of ruthenium, osmium, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold and silver are novel compounds.

35 In yet another embodiment of the sixth aspect of the present invention, the catalytic component, which is especially useful in metathesis reactions such as ROMP, as well as in atom or group transfer radical polymerisation (ATRP) of one or more radically (co)polymerisable monomers, atom transfer radical addition (ATRA) and vinylation reaction, may also be a tetra-coordinated or penta-coordinated metal complex, a salt, a solvate or an enantiomer thereof, wherein the metal is
40 selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten,

titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt, the said metal complex comprising:

- at least one bidentate phosphine ligand, and
- 5 - at least one other ligand being selected from solvent ligands (in which case the complex is a cationic species associated with an anion), anionic ligands and non-anionic ligands.

Bidentate phosphine ligands suitable for inclusion in the above metal complex have been extensively disclosed in U.S. Patent No. 6,037,500, the content of which is incorporated herein by reference. An exemplary (but not limiting) bidentate phosphine ligand has the general formula (IIIC) shown in figure 3, wherein:

- each R is independently selected from the group consisting of C₁₋₇ alkyl and aryl, preferably phenyl, and
- each cyclic structure represents a ring having 3 to 8 carbon atoms, preferably cyclopentyl or cyclohexyl, which may be substituted within the ring with one or more atoms or groups independently selected from the group consisting of oxygen, sulfur, oxo, thioxo, NR₁₅ and C(R₁₅)₂, wherein R₁₅ is selected from the group consisting of C₁₋₇ alkyl, halo C₁₋₇ alkyl, aryl and arylalkyl.

As is taught in U.S. Patent No. 6,037,500, especially figures 3-5 and 7 thereof, the number of atoms between the phosphorus atoms of the two phosphine groups of the said bidentate ligands is not necessarily 4 as shown in formula (IIIC) but may also be 3 (spiro phosphines) or 2 (in which case the phosphorus atoms of the two phosphine groups may be linked with each other through a bismethylene or arylene, preferably phenylene, linking group) or else may be higher than 4 (for instance with the said phosphorus atoms being linked with each other through a ferrocene group).

In particular, the metal complex of this embodiment may include two bidentate phosphine ligands, the said metal complex then being a cationic species associated with an anion (which may be selected from the group consisting of tetrafluoroborate, tetra(pentafluorophenyl)borate, perchlorate, antimoniohexafluoride, alkylsulfonates wherein the alkyl group may be substituted with one or more halogen atoms such as trifluoromethanesulfonate, and arylsulfonates). Such complexes are novel and may easily be made by reacting at least 2 moles of the bidentate phosphine ligand with one mole of a cationic metal complex including two non-anionic bidentate ligands such as L³ described hereinabove, in association with the aforesaid anion.

Alternatively, the metal complex of this embodiment may include a single bidentate phosphine ligand in association with either (i) two solvent ligands (which may be selected from the group consisting of protic solvents, polar aprotic solvents and non-polar solvents, including aromatic hydrocarbons, chlorinated hydrocarbons, ethers, aliphatic hydrocarbons, alcohols, esters, ketones, amides and water) or (ii) two anionic ligands such as L⁴ described hereinabove and optionally a non-anionic ligand such as an aryl group or (iii) a single anionic ligand such as L⁴ described hereinabove (in which case the said metal complex is then a cationic species associated with an anion such as described above) or (iv) a single non-anionic bidentate ligand such as L³ (in which case the said metal complex is then a cationic species associated with an anion A such as

decribed above). All of the latter alternatives are novel complexes when the metal is selected from the group consisting of osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt. The alternative (i) hereinabove also relates to novel complexes when the metal is
5 selected from the group consisting of rhodium, ruthenium, palladium and platinum.

The catalysts of the present invention thus have utility in the whole range of chemical reactions and processes listed and explained in detail hereinbefore. Due to this advantageous versatility, they may be used in the manufacture of intermediates in a variety of agrochemicals or therapeutically active substances belonging to various therapeutic classes such as, but not limited
10 to, naproxen (an anti-inflammatory agent); prostaglandins; alkaloids; morphine and salts thereof; morphine analogues including morphinan, benzylmorphin and methoxy-N-methylmorphinan (dextromethorphan); levamisole (an anthelmintic); levofloxacin; indinavir (a HIV protease inhibitor); or intermediates in a variety of synthetic fragrances such as, but not limited to, citronellol.

In a seventh aspect, the invention further provides an at least penta-coordinated metal complex,
15 a salt, a solvate or an enantiomer thereof, comprising:

- a tetradentate ligand comprising two Schiff bases, wherein the nitrogen atoms of said two Schiff bases are linked with each other through a C₁₋₇ alkylene or arylene linking group A; and
- one or more non-anionic ligands L⁷ selected from the group consisting of (i) imidazoles and
20 trisubstituted phosphines PR₃ wherein R is a radical selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl; and (ii) aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro,
25 cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.

Each of the substituting radicals R and the ligand L⁷ may, independently from each other, be any of the above-mentioned groups with any of the substituents listed for such groups, including any of the individual meanings for such groups or substituents which are listed in the definitions
30 given hereinabove. Preferably the non-anionic ligand L⁷ has constraint steric hindrance such as, but not limited to, mono- or polysubstituted phenyl, e.g. xylyl, cumenyl, cymenyl or mesityl. Preferably the substituting radicals R also have constraint steric hindrance such as, but not limited to, phenyl or cyclohexyl.

The at least penta-coordinated metal complex according to this seventh aspect of the invention
35 preferably is a monometallic complex. Preferably the metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table. More preferably the said metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

In a specific embodiment of such at least penta-coordinated metal complexes, each said non-anionic ligand L^7 may be is cymene. The C_{1-7} alkylene or arylene linking group A may be substituted with one or more substituents preferably selected from the group consisting of chloro, bromo, trifluoromethyl and nitro. Preferably the C_{1-7} alkylene or arylene linking group A, together
 5 with the two linked nitrogen atoms, is derived from o-phenylenediamine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,6-diaminohexane or 1,7-diaminoheptane. Also preferably, each Schiff base of the tetradentate ligand is derived from salicylaldehyde or acetylacetone, wherein the salicylidene or acetylidene group included in each such Schiff base may be substituted with one or more substituents preferably selected from the
 10 group consisting of chloro, bromo, trifluoromethyl and nitro.

Suitable but non limiting examples of tetradentate ligands for this seventh aspect of the invention have one of the general formulae (IIA), (IIB) and (IIC) shown in figure 2. More specific examples include the so-called salen (i.e. bis(salicylaldehyde) ethylenediamine), saloph (i.e. bis(salicylaldehyde)o-phenylenediamine), hydroxy-acetoph, and accac (i.e. bis(acetylacetone)
 15 ethylenediamine) ligands, and substituted derivatives thereof. In formulae (IIA) and (IIC), the substituents X are preferably selected from the group consisting of chloro, bromo, trifluoromethyl and nitro. In formula (IIB), the substituents Y are preferably selected from the group consisting of chloro, bromo, trifluoromethyl and nitro, and the substituents X are preferably selected from the group consisting of hydrogen, methyl, fluoro, chloro, bromo, trifluoromethyl and nitro. In formula
 20 (IIA) the substituents Y are preferably selected from the group consisting of hydrogen and methyl. A preferred tetradentate ligand is *N,N'*-bis(5-nitro-salicylidene)-ethylenediamine. Other suitable ligands include *N,N'*-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine), 1,2-diphenylethylenebis(2-hydroxy-acetophenonylideneimine) and 1,1'-binaphtalene-2,2'-diaminobis(2-hydroxyaceto-phenonylideneimine), all being described in *Molecules* (2002) 7:511-516.

The at least penta-coordinated metal complex according to this seventh aspect of the invention may be made by reacting a suitable tetradentate ligand such as defined hereinabove with a preferably bimetallic complex of the desired metal, more preferably a homobimetallic complex wherein the desired metal is coordinated with a non-anionic ligand L^7 and at least one anionic ligand, such as $[RuCl_2(p\text{-cymene})]_2$, $[RuCl_2(COD)]_2$ or $[RuCl_2(NBD)]_2$, wherein COD and NBD
 25 respectively mean cyclooctadiene and norbornadiene.

In an eighth aspect, his invention also provides a catalytic system comprising:

- (a) as the main catalytic species, an at least penta-coordinated metal complex according to the seventh aspect described hereinabove, and
- (b) one or more co-catalysts or initiators for the main catalytic species.

The co-catalyst or initiator may be selected from amines, preferably secondary amines; organoaluminum compounds; and initiators having a radically transferable atom or group.

The initiator having a radically transferable atom or group may preferably be selected from the group of initiators having the formula $R_{35}R_{36}R_{37}CX_1$ wherein:

- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably

- vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C₁₋₆ alkyl groups and phenyl-substituted C₁₋₆ alkyl), SR₃₉, OC(=O)R₃₉, OP(=O)R₃₉, OP(=O)(OR₃₉)₂, OP(=O)OR₃₉, O-N(R₃₉)₂ and S-C(=S)N(R₃₉)₂, wherein R₃₉ is aryl or C₁₋₂₀ alkyl, or where an N(R₃₉)₂ group is present, the two R₃₉ groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
- R₃₅, R₃₆ and R₃₇ are each independently selected from the group consisting of hydrogen, halogen, C₁₋₂₀ alkyl (preferably C₁₋₆ alkyl), C₃₋₈ cycloalkyl, C(=O)R₄₀, (wherein R₄₀ is selected from the group consisting of C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, aryloxy or heteroaryloxy), C(=O)NR₄₁R₄₂ (wherein R₄₁ and R₄₂ are independently selected from the group consisting of hydrogen and C₁₋₂₀ alkyl or R₄₁ and R₄₂ may be joined together to form an alkylene group of 2 to 5 carbon atoms), COCl, OH, CN, C₂₋₂₀ alkenyl (preferably vinyl), C₂₋₂₀ alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C₂₋₂₀ alkenyl.

In a ninth aspect, this invention also provides a supported catalyst for use in a heterogeneous catalytic reaction, comprising:

- (a) a catalytically active at least penta-coordinated metal complex according to the seventh aspect or a catalytic system according to the eighth aspect described hereinabove, and
- (b) a supporting amount of a carrier suitable for supporting said catalytically active metal complex or catalytic system (a).

Said carrier may be selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins, all of them being as defined hereinabove with respect to the fifth aspect of the invention.

The at least penta-coordinated metal complex according to the seventh aspect of the invention is useful as a catalytic component in a reaction involving the transfer of an atom or group to an olefin or another reactive substrate. For instance the said reaction comprises the step of reacting the olefin or reactive substrate with a second substrate under suitable reaction conditions in the presence of the said catalytic component, the second substrate being a suitable donor for the atom or group to be transferred. More specifically, the said reaction may be, but without limitation, selected from the group consisting of:

- atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
- atom transfer radical addition (the latter being as explained in the background of the invention), e.g. the addition of a polyhalomethane having the formula CX_nH_{4-n}, wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to produce the corresponding saturated polyhalogenated adduct, including for instance the addition of carbon tetrachloride or chloroform onto an α -olefin;
- vinylation reaction, i.e. the reaction of a mono- or di-alkyne (e.g. phenylacetylene or 1,7-octadiyne) with a monocarboxylic acid (e.g. formic acid or acetic acid) or dicarboxylic acid

- to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti- Markovnikov adducts or mixtures thereof;
- cyclopropanation of an α -ethylenically unsaturated compound for producing an organic compound having one or more cyclopropane structural units;
 - 5 - quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
 - epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
 - oxidation of organic compounds including the oxidation of saturated hydrocarbons (such as, but not limited to, methane) for producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for
10 producing carboxylic acids;
 - cyclopropenation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
 - hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for
15 producing β -cyano carbonyl compounds;
 - hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
 - aziridination of imines or alkenes for producing organic compounds having one or more
20 aziridine structural units;
 - hydroamidation of olefins for producing saturated amides;
 - hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
 - aminolysis and hydroamination of olefins for producing saturated primary or secondary amines, and hydroamination of alkynes for producing unsaturated amines;
 - 25 - isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;
 - Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
 - hydroboration of olefins for producing alkylboranes and trialkylboranes;
 - hydride reduction of aldehydes and ketones for producing alcohols;
 - aldol condensation of saturated carboxyl compounds (aldehydes or ketones) for producing
30 α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intra-molecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds (aldehydes or ketones);
 - Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
 - 35 - Robinson annulation, i.e. Michael addition followed by an intramolecular aldol condensation, of a ketone onto an α,β -unsaturated carboxyl compound for producing saturated polycyclic carboxyl compounds being suitable intermediates for steroids and other natural products containing six-membered rings;

- Heck reactions, i.e. the reaction of an aryl halide or a 1-hetero-2,4-cyclopentadiene (or a benzo-fused derivative thereof) with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
- codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
- hydroxylation of olefins for producing alcohols;
- alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones;
- Diels-Alder reactions such as, but not limited to, the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbornenes;
- Suzuki-Miyaura cross-coupling reactions;
- silylmatalation of unsaturated compounds, particularly olefins and carbonyl compounds;
- and
- carbometalation reactions of silyl cyanides and allyl silanes with carbonyl compounds and olefins.

Each of the above synthetic reactions should be understood as expressed in detail hereinabove with respect to the sixth aspect of the present invention.

In still another aspect, this invention provides useful catalysts species being penta-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- a bidentate Schiff base ligand (such as above defined),
- an anionic ligand (such as above defined),
- a non-anionic ligand (such as above defined), and
- a Fischer carbene ligand.

Fischer carbene ligands are well known in the art and are consistently defined, e.g. in <http://www.ilpi.com/organomet/carbene.html> and in <http://www.chemistry.ucsc.edu/~claudel/Fischer.html>, as including a pi-donor group. Preferably in this aspect of the present invention, said pi-donor group should be selected from the group consisting of C₁₋₇ alkoxy, C₃₋₁₀ cycloalkoxy, aryloxy, arylalkyloxy, heterocyclic-substituted alkyloxy, thio C₁₋₇ alkyl, thio C₃₋₁₀ cycloalkyl, thioaryl, arylalkylthio and heterocyclic-substituted alkylthio. More preferably the Fischer carbene ligand in this aspect of the present invention should be a C₁₋₇ alkoxyvinylidene, most preferably ethoxyvinylidene. Preferably in this aspect of the present invention, the bidentate Schiff base ligand has one of the general formulae (IA) or (IB) referred to in figure 1, wherein:

- Z is selected from the group consisting of oxygen, sulphur, selenium, NR^{'''}, PR^{'''}, AsR^{'''} and SbR^{'''}, wherein R^{'''} is a radical selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- R^{''} and R^{'''} are each a radical independently selected from the group consisting of hydrogen, C₁₋₆ alkyl, C₃₋₈ cycloalkyl, aryl and heteroaryl, or R^{''} and R^{'''} together form an aryl

or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-7} alkyl, C_{1-7} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, alkylammonium and arylammonium; and

- 5 - R' is either as defined for R'' and R''' when included in a Schiff base having the general formula (IA) or, when included in a Schiff base having the general formula (IB), is selected from the group consisting of C_{1-7} alkylene and C_{3-10} cycloalkylene, the said alkylene and cycloalkylene group being optionally substituted with one or more substituents R_5 .

Preferably in this aspect of the present invention, the non-anionic ligand is selected from the group consisting of trisubstituted phosphines PR_3 wherein R is a radical selected from the group consisting of C_{1-7} alkyl, C_{3-10} cycloalkyl, aryl and heteroaryl. Also preferably in this aspect of the present invention, the anionic ligand is selected from the group consisting of C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-7} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium, arylammonium, alkylidicketonate, arylidicketonate, halogen, nitro and cyano.

Representative examples of Fischer carbene containing penta-coordinated metal complexes include, but are not limited to, complexes such as:

- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium,
- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-5-nitro)-1-phenyl)iminomethane]-ruthenium,
- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium,
- toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate,
- toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-5-nitro)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate, and
- toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate.

Such Fischer carbene containing penta-coordinated metal complexes proved to be efficient as catalytic components for performing reactions involving the transfer of an atom or group to an olefin or another reactive substrate (such reactions being as illustrated above), especially in the atom transfer radical polymerisation of monomers like styrene and (meth)acrylates.

In still another aspect, this invention provides useful catalysts species being penta-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- (a) an anionic ligand (such as above defined),
- (b) a non-anionic ligand (such as above defined),
- (c) a carbene ligand, and

(d) a bidentate Schiff base ligand having one of the general formulae (IA) or (IB) referred to in figure 1, wherein:

- Z is selected from the group consisting of $\text{NR}^{\text{'''}}$, $\text{PR}^{\text{'''}}$, $\text{AsR}^{\text{'''}}$ and $\text{SbR}^{\text{'''}}$, wherein $\text{R}^{\text{'''}}$ is a group containing a terminal silyl moiety such as, but not limited to, (tri C_{1-7} alkoxy)silyl) C_{1-7} alkyl;
- $\text{R}^{\text{''}}$ and $\text{R}^{\text{'''}}$ are each a radical independently selected from the group consisting of hydrogen, C_{1-6} alkyl, C_{3-8} cycloalkyl, aryl and heteroaryl, or $\text{R}^{\text{''}}$ and $\text{R}^{\text{'''}}$ together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-7} alkyl, C_{1-7} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, alkylammonium and arylammonium; and
- R' is either as defined for $\text{R}^{\text{''}}$ and $\text{R}^{\text{'''}}$ when included in a Schiff base having the general formula (IA) or, when included in a Schiff base having the general formula (IB), is selected from the group consisting of C_{1-7} alkylene and C_{3-10} cycloalkylene, the said alkylene and cycloalkylene group being optionally substituted with one or more substituents R_5 .

As illustrated in the examples below, metal complexes according to this aspect of the present invention may be monometallic or bimetallic. They may also be grafted to a suitable carrier such as a porous inorganic solid. Metal complexes according to this aspect of the present invention proved to be efficient as catalytic components for performing olefin or acetylene metathesis reactions such as, but not limited to, RCM and ROMP.

In still another aspect, this invention provides useful catalysts species being penta-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- (e) an anionic ligand (such as above defined),
- (f) a non-anionic ligand (such as above defined),
- (g) a bidentate Schiff base ligand, and
- (h) a carbene ligand having a terminal hydrocarbylsilyl group such as, but not limited to, trialkylsilyl (e.g. trimethylsilyl), triarylsilyl and tricycloalkylsilyl.

Metal complexes according to this aspect of the present invention proved to be efficient as catalytic components for performing olefin or acetylene metathesis reactions such as, but not limited to, RCM and ROMP.

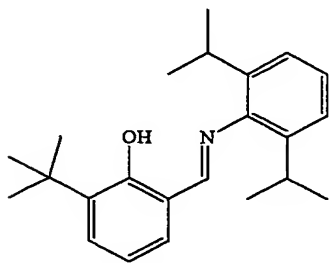
The present invention will now be further explained by reference to the following set of examples which should be understood as merely illustrating various embodiments of the invention without limiting the scope thereof.

EXAMPLES 1-A to 1-E - preparation of Schiff base ligands

Schiff base ligands were prepared and purified as follows. Condensation of a salicylaldehyde (10 mmole) with a suitably substituted aniline was carried out with stirring in 40 ml methanol at reflux temperature during 4 hours. After cooling at -18°C for 24 hours, the crystals formed were filtered and washed with cold ethanol, then dried *in vacuo* at 40°C during 4 hours to afford with the following yields the desired salicylaldimine ligands. Each ligand (formula given hereunder) was

characterized by means of proton nuclear magnetic resonance (hereinafter referred as NMR, performed at 300 MHz with C₆D₆ at 25°C), carbon NMR (performed at 75 MHz with C₆D₆) and infrared spectrophotometry (IR, performed with CCl₄), as follows:

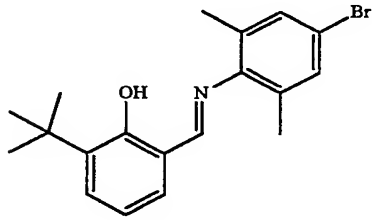
- N-(2,6-diisopropylphenyl)-2-hydroxy-3-tertbutyl-1-phenylmethaneimine (Schiff base 1-A) obtained (yellow-orange oil, 2.9 g, yield 87 %) from 1.71 ml 3-*tert*-butyl-2-hydroxybenzaldehyde and 1.88 ml 2,6-diisopropylaniline.



¹H-NMR: δ 12.24 (s, 1H), 9.19 (s, 1H), 7.34-6.67 (m, 6H), 2.96 (sept, 2H), 1.56 (s, 9H) and 1.31 (d, 12H) ppm; ¹³C-NMR: δ 167.4, 160.3, 146.0, 138.8, 137.5, 130.4, 125.3, 123.0, 118.6, 118.3, 109.2, 34.9, 28.0 and 23.2 ppm; IR: 3451 (OH), 3056, 2962 (tBu), 2927, 2870, 1626 (C=N), 1579, 1494, 1437, 1396, 1385, 1359, 1318, 1278, 1109, 1060, 906, 844, 813, 781, 759, 741, 701, 560 and 462 cm⁻¹.

A

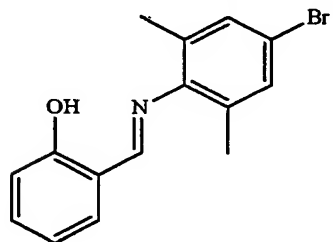
- N-(4-bromo-2,6-dimethylphenyl)-2-hydroxy-3-tertbutyl-1-phenylmethaneimine (Schiff base 1-B) obtained (yellow oil, 2.8 g, yield 79 %) from 1.71 ml 3-*tert*-butyl-2-hydroxybenzaldehyde and 2 g 4-bromo-2,6-dimethylaniline.



¹H-NMR: δ 12.35 (s, 1H), 8.3 (s, 1H), 7.45 (d, 1H), 7.25 (s, 2H), 7.18 (d, 1H), 6.9 (t, 1H), 2.15 (s, 6H) and 1.6 (s, 9H) ppm; ¹³C-NMR: δ 168.2, 161.3, 147.3, 139.0, 138.0, 130.9, 126.3, 123.9, 118.7, 118.0, 110.1, 35.1, 28.5, 23.8 ppm; IR: 3450 (OH), 3057, 2964 (tBu), 2928, 2888, 1627 (C=N), 1578, 1496, 1438, 1386, 1360, 1320, 1280, 1212, 1174, 1109, 1097, 1061, 989.7, 844, 813, 800, 782, 759,

739, 701, 623, 560, 534, 462 and 418 cm⁻¹.

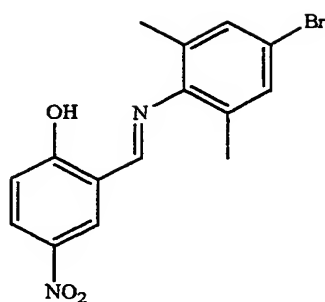
- N-(4-bromo-2,6-dimethylphenyl)-2-hydroxy-1-phenylmethaneimine (Schiff base 1-C) obtained (yellow powder, 2.83 g, yield 93 %) from 1.065 ml salicylaldehyde and 2 g 4-bromo-2,6-dimethylaniline.



¹H-NMR: δ 12.85 (s, 1H), 8.32 (s, 1H), 7.30-7.15 (m, 6H) and 2.21 (s, 6H) ppm; ¹³C-NMR: δ 167.0, 160.9, 148.3, 138.9, 133.4, 132.1, 130.8, 130.3, 119.0, 117.6, 117.2 and 19.0 ppm; IR: 3350, 3065, 3031, 2942, 2930, 2860, 1620 (C=N), 1570, 1526, 1489, 1461 and 1109 cm⁻¹.

C

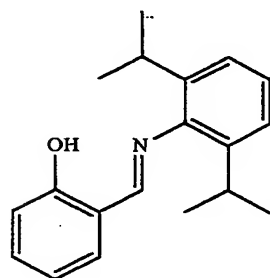
- N-(4-bromo-2,6-dimethylphenyl)-2-hydroxy-4-nitro-1-phenylmethaneimine (Schiff base 1-D) obtained as a dark yellow powder from 1.67 g 4-hydroxy-3-nitrobenzaldehyde and 2 g 4-bromo-2,6-dimethylaniline.



D

$^1\text{H-NMR}$: 13.96 (s, 1H), 8.41 (s, 1H), 8.35 (d, 1H), 8.30 (d, 1H), 7.28 (s, 2H), 7.13 (d, 1H) and 2.19 (s, 6H) ppm; $^{13}\text{C-NMR}$: δ 166.4, 165.5, 145.6, 139.8, 132.0, 130.4, 128.7, 128.5, 118.6, 118.3, 117.1, and 18.1 ppm; IR: 3459 (OH), 3086, 3059, 2987, 2967, 2932, 1619 (C=N), 1581, 1523, 1480, 1458, 1340 (NO_2), 1300, 1177, 1095, 983, 937, 853, 832, 798, 772, 751, 731, 716, 659, 633, 567 and 464 cm^{-1} .

- 10 - N-(2,6-diisopropylphenyl)-2-hydroxy-4-nitro-1-phenylmethanimine (Schiff base 1-E) obtained as a yellow powder from 1.065 ml salicylaldehyde and 1.88 ml 2,6-diisopropylaniline.



E

$^1\text{H-NMR}$: 13.16 (s, 1H), 8.34 (s, 1H), 7.46 (d, 1H), 7.40 (t, 1H), 7.22 (bs, 3H), 7.10 (d, 1H), 6.99 (t, 1H), 3.20 (sept, 2H) and 1.20 (d, 12H) ppm; $^{13}\text{C-NMR}$: δ 166.4, 161.0, 145.9, 138.4, 133.0, 132.0, 125.3, 123.0, 118.8, 118.4, 117.1, 27.9 and 23.3 ppm; IR 3330 (OH), 3080, 3055, 2982, 2970, 2930, 1608 (C=N), 1581, 1520, 1477, 1454, 1323, 1301, 1170, 1090, 980, 935, 850, 835, 796, 770 and 751 cm^{-1} .

EXAMPLES 2 to 8 - preparation of Schiff base substituted ruthenium complexes

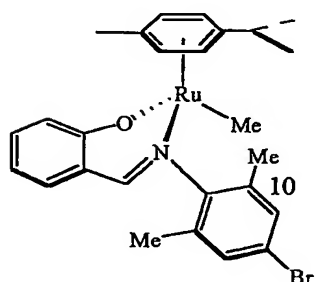
- 25 Ruthenium complexes with Schiff bases from examples 1-A to 1-E were prepared in three steps and purified as follows. In a first step, to a solution in THF (15 ml) of the appropriate Schiff base (3 mmole), a solution of thallium ethoxide in THF (5 ml) was added dropwise at room temperature. Immediately after addition, a pale yellow solid was formed and the reaction mixture was stirred for 2 hours at 20°C .

- 30 To a solution of the said salicylaldehyde thallium salt in THF (5 ml) was added a solution of $[\text{RuCl}_2(\text{p-cymene})]_2$ in THF (5 ml), then the reaction mixture was stirred at room temperature (20°C) for 6 hours. The thallium chloride by-product was removed via filtration. After evaporation of the solvent, the residue was recrystallized at 0°C from a dichloromethane/pentane mixture. The resulting product was then dissolved in dry ether (15 ml) and cooled down to 0°C .

- 35 In a third and last step, to the said ether solution was slowly added a solution of methyllithium (2.3 ml, 1.4 M in ether) or phenylmagnesium chloride (1.75 ml, 2 M in THF) or pentafluorophenylmagnesium chloride (7 ml, 0.5 M in ether), respectively. The reaction mixture was then slowly warmed up the room temperature and was stirred for 4 hours. The salt formed was filtered and the solvent removed. After recrystallization from ether/pentane, complexes having the following formulae were obtained with yields ranging from 60 to 70% and characterized by means

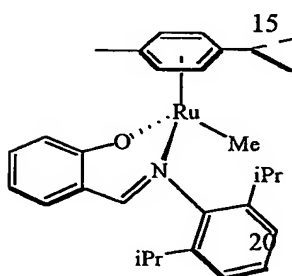
of proton nuclear magnetic resonance (hereinafter referred as NMR, performed at 300 MHz with C_6D_6 at 25°C), carbon NMR (performed at 75 MHz with C_6D_6) and infrared spectrophotometry (IR, performed with CCl_4), as follows:

- 5 - example 2 (obtained from Schiff base 1-C and methyllithium):



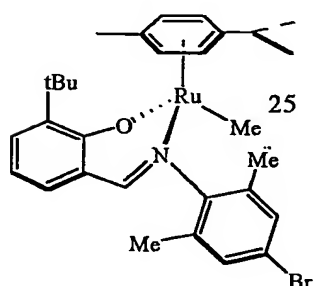
1H -NMR: 9.81 (s, 1H), 7.10-6.80 (m, 6 H), 1.33 (s, 6H); 5.48 (d, 1H), 5.34 (d, 1H), 4.48 (d, 1H), 4.36 (d, 1H), 2.90 (sept, 1H), 2.16 (s, 3H), 1.26 (d, 6H) and 0.10 (s, 3H) ppm; IR (KBr) 3051, 2957, 2923, 2853, 1920, 1670, 1596, 1564, 1516, 1462, 1447, 1372, 758 cm^{-1}

- example 3 (obtained from Schiff base 1-E and methyllithium):



1H -NMR: 9.70 (s, 1H), 7.3-7.0 (m, 7 H), 3.00 (sept, 2H), 1.12 (d, 12 H); 5.43 (d, 1H), 5.30 (d, 1H), 4.47 (d, 1 H), 4.33 (d, 1H), 3.10 (sept, 1H), 2.11 (s, 3H), 1.22 (d, 6H) and 0.22 (s, 3H) ppm; IR: 3052, 2980, 2970, 2924, 1602, 1583, 1514, 1470, 1451, 1333, 1300, 1087, 976, 930, 850, 830, 796 and 750 cm^{-1}

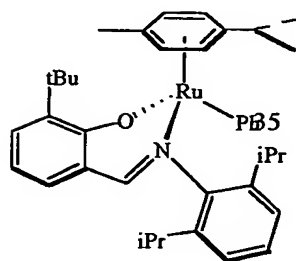
- example 4 (obtained from Schiff base 1-B and methyllithium):



1H -NMR: 9.27 (s, 1H), 7.2-7.75 (m, 6 H), 3.00 (sept, 2H), 1.12 (d, J = 6.5 Hz, 12 H); 5.43, 4.70 4.44, 4.37, (d, 4H), 3.14 (sept, 1H), 2.08 (s, 3H), 1.30 (d, 6H) and 0.13 (s, 3H) ppm; IR: 3052, 2980, 2970, 2924, 1602, 1583, 1514, 1470, 1451, 1333, 1300, 1087, 976, 930, 850, 830, 796 and 750 cm^{-1}

30

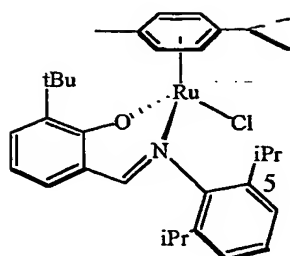
- example 5 (obtained from Schiff base 1-A and phenylmagnesium chloride):



1H -NMR: 9.70 (s, 1H), 7.3-7.0 (m, 7 H), 3.00 (sept, 2H), 1.12 (d, J = 6.5 Hz, 12 H); 5.43 (d, 2H), 5.30(d, 2H), 3.10 (sept, 1H), 2.11 (s, 3H), 1.22 (d, 6H) and 0.22 (s, 3H) ppm; IR: 3052, 2980, 2970, 2924, 1602, 1583, 1514, 1470, 1451, 1333, 1300, 1087, 976, 930, 850, 830, 796 and 750 cm^{-1}

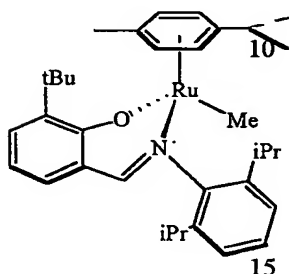
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- example 6 (obtained from Schiff base 1-A in the second step)



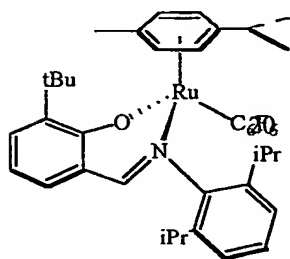
$^1\text{H-NMR}$ 7.69 (s, 1H), 7.07-6.12 (m, 6H), 2.99 (sept, 2H), 1.40 (s, 9H), 1.28 (d, 12H); 5.10, 4.55, 4.46, 4.39 (d, 1H), 2.72 (sept, 1H), 1.60 (s, 6H) and 1.09 (d, 6H) ppm; $^{13}\text{C-NMR}$: 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47, 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40 and 17.86 ppm; IR: 3050, 3032, 2956, 2923, 2853, 1920, 1672, 1594, 1536, 1467, 1447, 1376, 1347 and 757 cm^{-1} .

- example 7 (obtained from Schiff base 1-A and methyllithium)



$^1\text{H-NMR}$: δ 7,693 (s, 1H); 7,047-6,15 (m, 6H); 2,723 (sept, 2H); 1,404 (s, 9H); 1,31 (d, 12H); 4,95 (d, 1H); 4,55 (d, 1H); 4,48 (d, 1H); 4,42 (d, 1H); 2,426 (sept, 1H); 1,596 (s, 3H); 1,050 (d, 6H) and 0,04 (s, 3H) ppm; $^{13}\text{C-NMR}$: δ 163,047; 152,815; 137,314; 134,565; 131,872; 127,227; 124,148; 122,06; 115,546; 35,619; 26,934; 103,04; 91,77; 88,36; 85,972; 79,485; 77,121; 30,837; 21,986 and 18,01 ppm.

- example 8 (obtained from Schiff base 1-A and pentafluorophenylmagnesium chloride)



$^1\text{H-NMR}$: 7.71 (s, 1H), 6.99-6.14 (m, 6H), 2.77 (sept, 2H), 1.46 (s, 9H), 1.30 (d, 12H); 5.20, 4.72, 4.58, 4.36 (all d, 1H), 2.61 (sept, 1H), 1.62 (s, 6H) and 1.10 (d, 6H) ppm; $^{13}\text{C-NMR}$ 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47, 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40, 17.86, 109.94(d), 136.51 (d), 133.19 (d) and 147.73 (d) ppm; IR: 3050, 3032, 2956, 2923, 2853, 1920, 1648, 1605, 1537, 1503, 1465, 1433, 1410, 1376, 1347, 1263, 1078, 1030, 801, 749, 720 and 566 cm^{-1}

25

EXAMPLE 9 – ring opening metathesis polymerisation

Ring opening metathesis polymerisation of various norbornene derivatives was performed during 17 hours at 85°C in toluene as a solvent, while using the Schiff base substituted ruthenium complexes of examples 4 and 5 as catalysts in a molar ratio monomer/catalyst equal to 225. The following table 1 indicates the name of the norbornene derivative and the polymerisation yield (expressed in %) achieved (ND: not determined) for each complex used.

30

Table 1

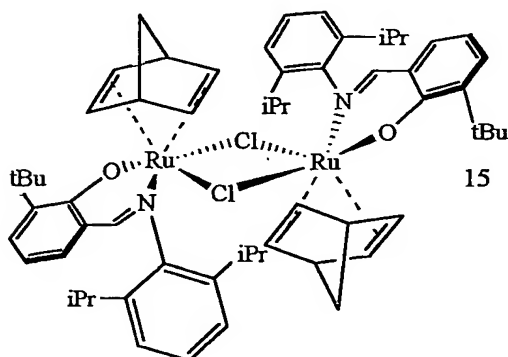
Monomer	Complex 4	Complex 5
norbornene	71	100
ethylnorbornene	57	100
butylnorbornene	47	100
hexylnorbornene	52	100
decylnorbornene	41	100

ethylidenenorbornene	9	83
cyclohexenylnorbornene	24	51
chloromethylnorbornene	36	65
triethoxysilylnorbornene	ND	95
hydroxymethylnorbornene	44	80

EXAMPLES 10 and 11 – preparation of bimetallic ruthenium complexes

A ruthenium precursor $[\text{RuCl}_2\text{L}^3]_2$, wherein L^3 is norbornadiene (example 10) or cyclooctadiene (example 11) was dissolved in methylene chloride (15 ml), to which was added 3 ml of the thallium salt of the Schiff base 1-A (10 ml, 0.3 m) and the reaction mixture was stirred for 10 hours. After thallium chloride filtration and solvent removal, the residue was washed with methylene chloride and characterized by means of proton nuclear magnetic resonance (hereinafter referred as NMR, performed at 300 MHz with C_6D_6 at 25°C), carbon NMR (performed at 75 MHz with C_6D_6) and infrared spectrophotometry (IR, performed with CCl_4), as follows:

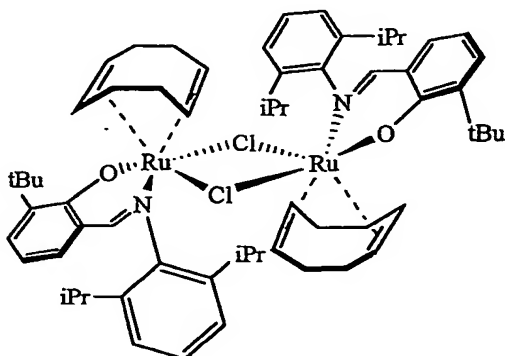
- example 10:



$^1\text{H-NMR}$: 7.70 (s, 1H), 7.14-6.66 (m, 6H), 2.70 (sept, 2H), 1.34 (s, 9H), 1.27 (d, 12H); 6.59 (d, 1H), 6.47 (d, 1H), 4.1 (s, 1H), 3.98 (s, 1H), 3.91 (s, 1H), 3.86 (s, 1H) and 1.82 (s, 2H) ppm; $^{13}\text{C-NMR}$ δ 160.98, 151.36, 140.15, 135.14, 130.91, 126.68, 123.88, 120.52, 113.92, 34.49, 31.17, 27.84, 24.59, 145.88, 140.15, 139.84, 135.14, 72.7, 54.94 and 50.10 ppm; IR: 3098, 3025, 3032, 2956, 2923, 2853, 1920, 1672, 1594,

1536, 1467, 1409, 1310, 1240, 1180, 1160, 1085, 1035, 1000, 941, 863, 805 and 757 cm^{-1} .

- example 11: $^1\text{H-NMR}$ 7.69 (s, 1H), 7.07-6.12 (m, 6H), 2.99 (sept, 2H), 1.40 (s, 9H), 1.28 (d, 12H); 5.10, 4.55, 4.46, 4.39 (all d, 1H), 2.72 (sept, 1H), 1.60 (s, 6H), 1.09 (d, 6H); $^{13}\text{C-NMR}$: 161.4, 152.9, 138.96, 133.36, 130.85, 125.74, 123.43, 118.7, 114.42, 35.34, 28.42, 26.52, 23.47, 104.14, 93.64, 86.38, 83.74, 80.69, 78.61, 30.20, 22.40 and 17.86 ppm; IR: 3050, 3032, 2956, 2923, 2853, 1920, 1672, 1594, 1536, 1467, 1447, 1376, 1347 and 757 cm^{-1} .



EXAMPLE 12 – ring opening metathesis polymerisation of norbornene

Ring opening metathesis polymerisation of norbornene was performed during 18 hours at 85°C in methylene chloride as a solvent, while using the Schiff base substituted ruthenium complexes of examples 6 to 8 and the bimetallic Schiff base substituted ruthenium complexes of examples 10 and 11 as catalysts in a molar ratio norbornene/catalyst equal to 225, and optionally in the presence of a co-catalyst being either triethylaluminum or diethylaluminum chloride (in a molar ratio 6:1 with respect to ruthenium) or an activator being trimethylsilyldiazomethane (TMSD, in a molar ratio 3:1 with respect to ruthenium). The following table 2 indicates the polymerisation yield (%) achieved (ND: not determined) for each complex used.

TABLE 2

Co-catalyst	Complex 6	Complex 7	Complex 8	Complex 10	Complex 11
without	52	32	76	50	69
AlEt ₃	76	86	72	68	75
AlEt ₂ Cl	75	100	100	87	88
TMSD	ND	66	77	81	ND

The norbornene polymer obtained in the presence of the complex of example 8 and diethylaluminum chloride was analysed and found to have a number average molecular weight of 450,000 and a molecular weight distribution (polydispersity) of 2.1.

EXAMPLE 13 – ring opening metathesis polymerisation of norbornene under irradiation

The experiment of example 12 is repeated with the ruthenium complex of example 8 without any co-catalyst or activator but at 20°C under irradiation by a source of visible light. The polymerisation yield observed after 20 hours is 86%.

EXAMPLE 14 – monometallic ruthenium complex coordinated with a nitrosubstituted salen ligand

A monometallic ruthenium complex coordinated with a *N,N'*-bis(5-nitro-salicylidene)-ethylenediamine ligand was made according to the general method disclosed above from a ruthenium precursor [RuCl₂L³]₂, wherein L is cymene. This complex was then tested in the atom transfer radical polymerisation of various olefins performed in 1 ml toluene during 17 hours at 85 °C (acrylates) or 110°C (styrene) while using:

- as an initiator, ethyl-2-methyl-2-bromopropionate (when the monomer is a methacrylate) or (1-bromoethyl)benzene (when the monomer is styrene), and
- a molar ratio [catalyst]/[initiator]/[monomer] equal to 1:2:800.

Table 3 indicates the name of the olefin involved, the polymerisation yield (expressed in %), the average number molecular weight M_n and the polydispersity index M_w/M_n .

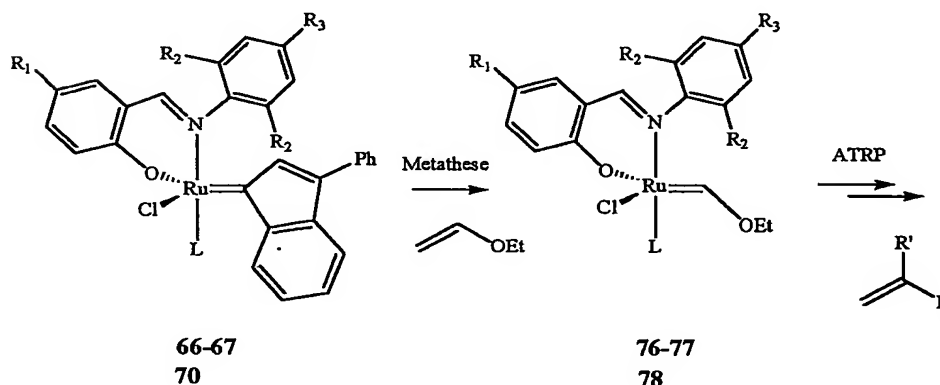
Table 3

Olefin	Yield	M _n	M _w /M _n
Methylmethacrylate (MMA)	69	41,000	2.2
Isobutylmethacrylate (IBMA)	83	59,000	2.4
Styrene (Sty)	67	26,000	1.7

EXAMPLES 15 to 17– preparation of Fischer carbene ruthenium complexes

Each of the following Fischer carbene ruthenium complexes was made in accordance with the following scheme by treating the starting complex with ethylvinylether (in a 10:1 ratio) for 30 minutes at room temperature in toluene:

- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium (76, example 15),
- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy-5-nitro)-1-phenyl)iminomethane]-ruthenium (77, example 16), and
- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium (78, example 17).

**EXAMPLE 18 - atom transfer radical polymerisation**

Complexes of examples 15 to 17 were tested as in example 14. Results are given in table 4.

Table 4

Catalyst	15				16				17			
Substrate	yield [%]	M _n (x 10 ³) [g/mol]	M _w /M _n	f	yield [%]	M _n (x 10 ³) [g/mol]	M _w /M _n	f	yield [%]	M _n (x 10 ³) [g/mol]	M _w /M _n	f
MMA	71	29.5	1.25	0.97	74	28.9	1.22	1.02	99	41.4	1.30	0.97
IBMA	64	39.5	1.22	0.93	65	38.4	1.18	0.97	90	57.4	1.36	0.90
MA	61	33.4	1.24	0.63	60	34.7	1.25	0.60	86	32.6	1.34	0.91
BA	74	57.8	1.29	0.66	80	58.1	1.27	0.71	82	50.3	1.38	0.84
Styrene	58	27.3	1.19	0.89	63	26.4	1.10	0.99	87	43.8	1.31	0.83

MA: methyl acrylate; BA: butyl acrylate.

EXAMPLES 19 to 21— preparation of cationic Fischer carbene ruthenium complexes

Each of the following cationic Fischer carbene ruthenium complexes was made in accordance with the following scheme by treating the corresponding complex of example 15 to 17 with silver tetrafluoroborate (in a 1:1 ratio) in toluene:

- toluy-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate (76⁺, example 19),
- toluy-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy-5-nitro)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate (77⁺, example 20),
- toluy-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate (78⁺, example 21).

EXAMPLE 22 - atom transfer radical polymerisation of methyl methacrylate and styrene

Complexes of examples 19 to 21 were tested as in example 14. Results are given in table 5.

Table 5

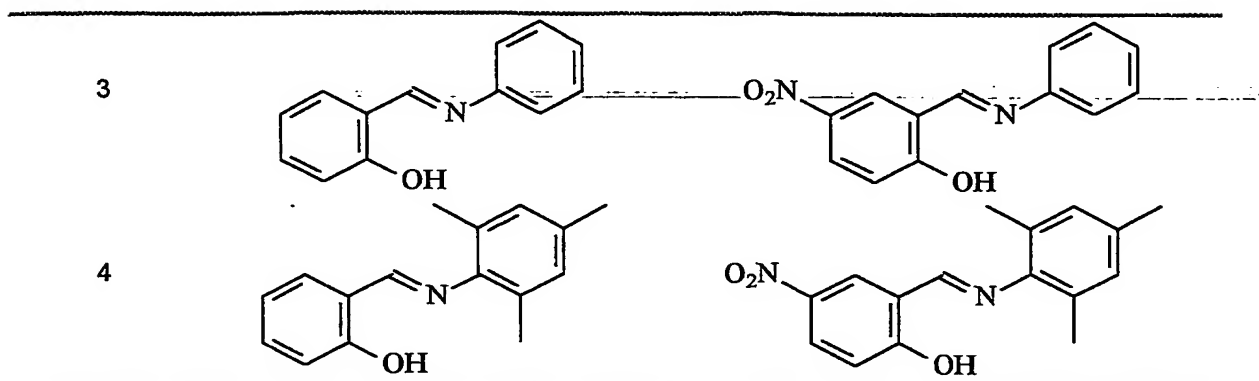
catalyst	76 ⁺				77 ⁺				78 ⁺			
Substrate	yield [%]	M _n (x 10 ³) [g/mol]	M _w /M _n	f	yield [%]	M _n ^c (x 10 ³) [g/mol]	M _w /M _n	f	yield [%]	M _n (x 10 ³) [g/mol]	M _w /M _n	f
MMA ^a	80	39.8	1.46	0.81	90	45.3	1.43	0.80	100	45.2	1.28	0.89
Styrene ^a	66	36.3	1.49	0.76	73	41.8	1.41	0.73	95	48.4	1.40	0.82
MMA ^b	88	59.0	1.58	0.60	99	64.3	1.57	0.62	100	49.1	1.40	0.82
Styrene ^b	74	54.3	1.51	0.57	81	58.4	1.55	0.58	100	52.3	1.56	0.80

EXAMPLE 23 – Schiff base ligands

The eight Schiff base ligands and nitro-ligands having the formulae shown in the following table 6 were prepared and purified according to the method described in example 1.

Table 6

Ref. N°	ligand	nitro-ligand
1		
2		



The ligand 1 (N-methyl-2-hydroxy-1-phenylmethanimine) was characterized by means of proton NMR, the corresponding spectrum being shown in figure 4.

5

EXAMPLES 24 to 33 - preparation of Schiff base substituted ruthenium complexes

Ruthenium complexes each having one Schiff base ligand or nitro-ligand from example 23, or the Schiff bases of examples 1-C and 1-D, and wherein ruthenium is also coordinated with a chloro atom and a p-cymene group, were prepared by performing the two first steps of the procedure described in examples 2-8. Each ruthenium complex was characterized by means of proton NMR performed with CDCl_3 at 25°C as follows:

- complex (example 24) obtained from the ligand 1 of example 23: δ at 8.35 (1H), 6.85-7.20 (4H), 3.12 (3H), 5.47 (2H), 5.34 (2H), 2.92 (1H), 2.17 (3H) and 1.25 (6H) ppm;
- complex (example 25) obtained from the ligand 2 of example 23: δ at 8.25 (1H), 6.85-7.00 (4H), 2.54 (9H), 5.46 (2H), 5.32 (2H), 2.75 (1H), 2.24 (3H) and 1.25 (6H) ppm;
- complex (example 26) obtained from the ligand 3 of example 23: δ at 7.76 (1H), 7.20-7.46 (4H), 6.92-7.02 (5H), 5.49 (2H), 5.34 (2H), 2.92 (1H), 2.16 (3H), and 1.25 (6H) ppm;
- complex (example 27) obtained from the ligand 4 of example 23: δ at 9.25 (1H), 6.75 (2H), 2.19 (3H), 2.13 (6H), 6.80-7.60 (4H), 5.39 (2H), 5.46 (2H), 2.77 (1H), 2.16 (3H) and 1.29 (6H) ppm;
- complex (example 28) obtained from the Schiff base of example 1-C: δ at 9.85 (1H), 7.24-7.44 (4H), 1.35 (6H), 6.94-7.07 (2H), 5.48 (2H), 5.36 (2H), 2.90 (1H), 2.16 (3H) and 1.26 (6H) ppm;
- complex (example 29) obtained from the nitro-ligand 1 of example 23: δ at 8.00 (1H), 6.86-7.49 (3H), 3.12 (3H), 5.47 (2H), 5.34 (2H), 2.92 (1H), 2.17 (3H) and 1.25 (6H) ppm;
- complex (example 30) obtained from the nitro-ligand 2 of example 23: δ at 8.10 (1H), 6.95-7.26 (3H), 2.54 (9H), 5.46 (2H), 5.32 (2H), 2.75 (1H), 2.24 (3H) and 1.25 (6H) ppm;
- complex (example 31) obtained from the nitro-ligand 3 of example 23: δ at 8.06 (1H), 7.39-7.61 (3H), 6.92-6.96 (5H), 5.49 (2H), 5.34 (2H), 2.92 (1H), 2.16 (3H) and 1.25 (6H) ppm;

- complex (example 32) obtained from the nitro-ligand 4 of example 23: δ at 8.80 (1H), 6.75 (2H), 2.19 (3H), 2.13 (6H), 6.85-7.50 (3H), 5.39 (2H), 5.46 (2H), 2.77 (1H), 2.16 (3H) and 1.29 (6H) ppm; and
- complex (example 33) obtained from the Schiff base of example 1-D: δ 8.00 (1H), 7.21-7.43 (3H), 1.35 (6H), 6.95-7.06 (2H), 5.48 (2H), 5.36 (2H), 2.90 (1H), 2.16 (3H) and 1.26 (6H) ppm.

EXAMPLE 34 – cyclopropanation of styrene with ethyldiazoacetate

The assymetric cyclopropanation of styrene with ethyldiazoacetate using one of the ruthenium complexes of examples 24 to 33 as a catalyst and toluene as a solvent, was performed while using the following amounts:

- catalyst: 5 μ mole,
 - ethyldiazoacetate: 625 μ mole, and
 - styrene: 12.5 mmole,
- i.e. a catalyst / diazo compound / olefin ratio of 1 / 125 / 2,500.

The catalyst was first dissolved in toluene, then styrene was added to the solution. Ethyl diazoacetate was dissolved in toluene and then added to the mixture of styrene and catalyst through a peristaltic pump over a period of 4 hours, after which the reaction mixture was heated to 60°C for 6 hours (with the following exceptions: heating time was increased to 10 hours when using the complexes of examples 28 and 30 as catalysts). After the reaction time, reaction products were analysed by gas chromatography, and conversion (expressed as a percentage) and diastereoselectivity (expressed as a cis:trans ratio) were calculated according to standard practice. Results are reported in table 7.

Table 7

Ru complex of example	24	25	26	27	28	30	31
Conversion (%)	78	82	99	91	75	67	95
cis : trans ratio	30:70	25:75	31:69	36:64	31:69	35:65	37:63

EXAMPLE 35 – oxidative cyclisation of 2-aminobenzyl alcohol with ketones

The oxidative cyclisation of 2-aminobenzyl alcohol with various ketones (i.e. the so-called modified Friedlaender quinoline synthesis) using one of the ruthenium complexes of examples 25 to 33 as a catalyst and dioxane as a solvent, was performed while using the following amounts:

- catalyst: 10 μ mole,
- 2-aminobenzyl alcohol: 1 mmole, and
- ketone: 2 mmoles,

i.e. an alcohol / catalyst ratio of 100 / 1.

A mixture of 2-aminobenzyl alcohol, ketone, catalyst and KOH (1 mmole) in dioxane (3 ml) was placed in a 5 ml screw-capped vial. The system was flushed with argon and allowed to react at 80°C for 1 hour. The reaction mixture was then filtered through a silica gel column (ethyl acetate),

washed with brine and dried over sodium sulfate. Removal of the solvent left a crude mixture which was separated by column chromatography (silica gel, ethyl acetate-hexane mixture) to give the relevant quinoline. Isolated yield (expressed as a percentage) based on 2-aminobenzyl alcohol is indicated in table 8 for each ketone and ruthenium complex used.

5

Table 8

ketone	Ru complex of example	Yield (%)
4-phenylcyclohexanone	25	97
acetophenone	27	100
cyclohexanone	27	100
cyclohexanone	28	98
3-methylacetophenone	33	100

EXAMPLE 36 - ring opening metathesis polymerisation in the presence of a co-catalyst at higher norbornene/catalyst molar ratios

10

Ring opening metathesis polymerisation of norbornene was performed as in example 12, in the presence of diethylaluminum chloride (in a molar ratio 6:1 with respect to ruthenium) as a co-catalyst, except that the norbornene/catalyst molar ratio was increased to 900 and 6,000 respectively, as shown in table 9 which also indicates the polymerisation yield (%) achieved (ND: not determined) for each complex used and each norbornene / catalyst ratio.

15

TABLE 9

Molar ratio	Complex 6	Complex 7	Complex 8	Complex 10	Complex 11
900	92	100	100	91	99
6,000	81	82	93	ND	ND

The norbornene polymers obtained in the presence of the complex of example 8 were analysed and found to have the following molecular weight M_n and polydispersity index M_w/M_n :

20

- at a norbornene/catalyst molar ratio of 900: M_n is 2,000,000 and M_w/M_n is 1.32;
- at a norbornene/catalyst molar ratio of 6,000: M_n is 1,350,000 and M_w/M_n is 1.33.

EXAMPLE 37 - ring opening metathesis polymerisation of norbornene in the presence of a co-catalyst at shorter reaction times

25

Ring opening metathesis polymerisation of norbornene was performed as in example 12, in the presence of diethylaluminum chloride (in a molar ratio 6:1 with respect to ruthenium) as a co-catalyst, except that reaction time was decreased to 30 minutes and 2 hours respectively, as shown in table 10 which also indicates the polymerisation yield (%) achieved for each complex used and each reaction time.

30

TABLE 10

Reaction time	Complex 6	Complex 7	Complex 8	Complex 10	Complex 11
30 minutes	29	37	94	42	53
2 hours	59	59	99	59	73

5 EXAMPLE 38 - ring opening metathesis polymerisation of strained cyclic olefins in the presence of a co-catalyst

Ring opening metathesis polymerisation was performed as in example 12, in the presence of diethylaluminum chloride (in a molar ratio 6:1 with respect to ruthenium) as a co-catalyst, except that norbornene was replaced as a monomer by the strained cyclic olefins shown in table 11 which also indicates the polymerisation yield (%) achieved for each complex used and each monomer.

TABLE 11

monomer	Complex 6	Complex 8	Complex 10	Complex 11
decylnorbornene	58	80	47	60
butylnorbornene	72	87	51	57
triethoxysilylnorbornene	77	69	41	62
ethyltetracyclododecene	100	38	84	100

15 EXAMPLE 39 - atom transfer radical polymerisation of MMA in the presence of a co-catalyst

The ruthenium complexes of examples 8, 10 and 11 were tested for the polymerisation of methyl methacrylate as in example 14, but in the presence of di-n-butylamine as an additive used in a molar ratio of 4:1 with respect to the ruthenium catalyst.

Table 12 indicates, for each complex used, the polymerisation yield (expressed in %), the average number molecular weight M_n and the polydispersity index M_w/M_n of the resulting polymer.

Table 12

Methyl methacrylate	Yield	M_n	M_w/M_n
Complex 8	100	194,000	1.51
Complex 10	53	59,000	1.50
Complex 11	56	49,000	1.51

25 EXAMPLE 40 - atom transfer radical polymerisation of styrene in the presence of a co-catalyst

The ruthenium complexes of examples 8, 10 and 11 were tested for the polymerisation of styrene as in example 14, but in the presence of di-n-butylamine as an additive used in a molar ratio of 4:1 with respect to the ruthenium catalyst.

Table 13 indicates, for each complex used, the polymerisation yield (expressed in %), the average number molecular weight M_n and the polydispersity index M_w/M_n of the resulting polymer.

Table 13

Styrene	Yield	M_n	M_w/M_n
Complex 8	100	49,000	1.83
Complex 10	99	53,000	1.77
Complex 11	66	38,000	1.86

EXAMPLE 41 - atom transfer radical polymerisation of styrene in the presence of a co-catalyst

The ruthenium complexes of examples 8, 10 and 11 were tested for the polymerisation of styrene as in example 14, but in the presence of tri-isopropylaluminum as an additive used in a molar ratio of 4:1 with respect to the ruthenium catalyst.

Table 14 indicates, for each complex used, the polymerisation yield (expressed in %), the average number molecular weight M_n and the polydispersity index M_w/M_n of the resulting polymer.

Table 14

Styrene	Yield	M_n	M_w/M_n
Complex 8	76	59,000	1.83
Complex 10	60	30,000	2.22
Complex 11	48	23,000	2.18

EXAMPLE 42 - vinylation reaction with a ruthenium catalyst

In a typical vinylation experiment, 4.4 mmole of a monocarboxylic acid (indicated in table 15), 4.4 mmole of a terminal alkyne (indicated in table 15) and 0.04 mmole of the ruthenium catalyst of example 6 were transferred into a 15 ml glass vessel containing 3 ml toluene. Then the reaction mixture was heated for 10 hours at 110°C under an inert atmosphere. The total yield was determined with Raman spectroscopy by following the decreasing intensity of the vibration $\nu_{C\equiv C}$ of the terminal alkyne and using a calibration curve. Reaction resulted in obtaining a mixture of products, the conformation of which was determined by proton NMR (using a spectrophotometer Varian Unity Inova 300 and the Varian software VNMR™, with TMS as a reference compound) and gas chromatography-mass spectrometry (hereinafter referred as GC-MS, using a gas chromatography apparatus Varian 4600 coupled with a mass spectrometer Finnigan MAT ITD, the chromatography column being a 30 m long silica capillar column commercially available from Supelco under the trade name SPB-5 with a diameter of 0.25 mm and a film thickness of 0.25 μ m, with a temperature program raising from 40°C up to 240°C at a rate of 5°C per minute, both FID detector and injector being at a temperature of 250°C). GC-MS measurements excluded the formation of other products than those reported below.

Results of these experiments are summarized in table 15, wherein M. stands for the percentage of Markovnikov product, (Z) anti-M. stands for the percentage of (Z) anti-Markovnikov product, (E) anti-M. stands for the percentage of (E) anti-Markovnikov product and enyns stands for the percentage of a mixture of dimerisation products being enyns, respectively.

Table 15

alkyne	acid	yield	M.	(Z) anti-M.	(E) anti-M.	enyns
Phenylacetylene	Formic	80	20	5	75	0
Phenylacetylene	Acetic	85	10	3	7	80
1,7-octadiyne	Formic	70	71	11	18	0
1,7-octadiyne	acetic	67	76	10	14	0

EXAMPLE 43 – atom transfer radical polymerisation

Complexes were prepared, by analogy with a procedure described by Carter et al. in *Polyhedron* (1993) 12:1123, by reacting two equivalents of a saturated aliphatic monoamine (identified in table 9) with one equivalent of $[\text{RuCl}_2(\text{p-cymene})]_2$. These complexes were then tested in the polymerisation of methyl methacrylate (MMA) or styrene using the same conditions as in example 14, except reaction time which was 8 hours. Results are given in table 16 and illustrate the influence of the choice of the aliphatic amine on the yield, molecular weight and polydispersity of polymethylmethacrylate.

Table 16

amine	MMA			Styrene		
	Yield	M_n	M_w/M_n	Yield	M_n	M_w/M_n
t-butylamine	n.a.	n.a.	n.a.	44	100,000	1.96
diethylamine	46	89,000	1.99	49	84,000	2.03
dibutylamine	73	140,000	1.95	37	81,000	1.75
triethylamine	n.a.	n.a.	n.a.	50	96,000	1.82
piperidine	53	122,000	1.65	58	103,000	1.60

EXAMPLE 44 – preparation of a heterogeneous catalyst by anchoring a dichloro-*p*-cymenyl-amino ruthenium complex onto a mesoporous crystalline molecular sieve

The synthesis of this solid-supported catalyst was effected by a method similar to that shown in figure 7 of WO 03/062253. In a first step, the mesoporous crystalline molecular sieve MCM 41 (having a specific surface of 1220 m²/g) was reacted with aminopropyltriethoxysilane at 100°C in the presence of toluene as a solvent. Then, in a second step, the resulting intermediate was reacted with $[\text{RuCl}_2(\text{p-cymene})]_2$ in the presence of methylene chloride as a solvent, thus yielding, after solvent removal, a supported catalyst being a dichloro-*p*-cymenyl-amino ruthenium complex anchored onto MCM 41.

EXAMPLE 45 - Atom transfer Radical Polymerisation in the presence of a supported catalyst

All reagents and solvents were dried, distilled and stored under nitrogen at – 20 °C with conventional methods. Then, 0.0116 mmole of the supported catalyst produced in example 37 was placed in a glass tube (in which the air was expelled by three vacuum-nitrogen cycles) containing a magnet bar and capped by a three-way stopcock. Then styrene (as the monomer) and 1-

bromoethyl benzene (as the initiator, diluted in toluene) were added to the catalyst in such amounts that the molar ratio [catalyst]/[initiator]/[monomer] was 1:2:800. All liquids were handled under argon with dried syringes. The reaction mixture was heated for 17 hours at 110°C and then, after cooling, diluted in chloroform and poured in 50 ml methanol under vigorous stirring, after which the precipitated polystyrene was filtered, dried under vacuum at 50°C during 4 hours and analysed. Polystyrene yield was 99%, molecular weight (M_n) was 77,000 and polydispersity index (M_w/M_n) was 1.68.

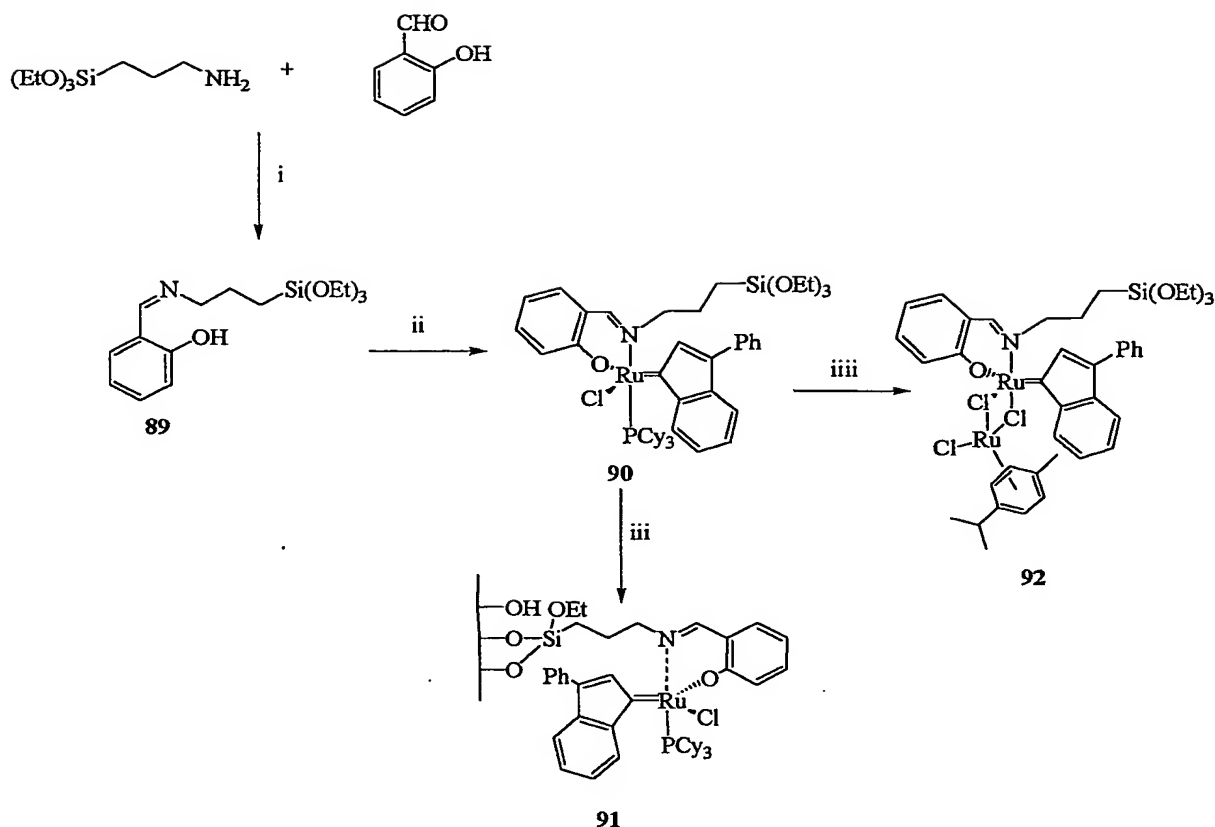
Repeating the same experiment with various methacrylates, but at a reaction temperature of 85°C and using ethyl-2-methyl-2-bromopropionate as the initiator, resulted in obtaining:

- a polymethylmethacrylate having a molecular weight (M_n) of 212,000 and a polydispersity index (M_w/M_n) of 1.64, with a yield of 86%, and
- a polyisobutylmethacrylate having a molecular weight (M_n) of 76,000 and a polydispersity index (M_w/M_n) of 1.70, with a yield of 100%.

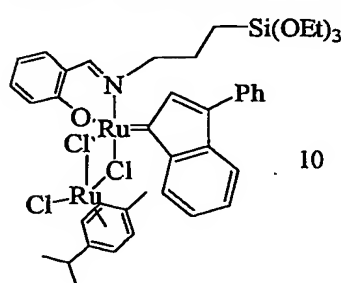
EXAMPLE 46 – preparation of ruthenium metal complexes wherein the Schiff base ligand contains a terminal silyl moiety

Ruthenium metal complexes wherein the Schiff base ligand contains a terminal silyl moiety were prepared according to the three-steps procedure shown in the following scheme. In the first step (i), a Schiff base ligand containing a terminal silyl (e.g. triethoxy-silyl) moiety was prepared by reacting 3-triethoxypropylamine with 2-hydroxybenzaldehyde during 2 hours at 25 °C in THF as a solvent. The resulting Schiff base ligand was then reacted at room temperature in step (ii) with thallium ethoxide during 1 hour and then with dichloro-(3-phenyl-1-indenylidene)-bis(tricyclohexylphosphino)-ruthenium during 4 hours.

75



The resulting monometallic ruthenium complex [90] was then transformed in step (iii) into a heterogeneous catalyst [91] by reaction at 25 °C with dry MCM-41 in methylene chloride during 24 hours, or in step (iv) into a bimetallic ruthenium complex [92] by the addition of 0.5 molar equivalent of [RuCl₂(p-cymene)]₂. The latter complex [92] was further characterised by proton and carbon nuclear magnetic resonance as follows:

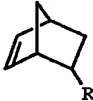



¹H NMR (300 MHz, CDCl₃): 8.52 (d, 1H), 8.30 (s), 7.78-6.98 (br m, 13H), 5.64, 5.52, 5.33, 5.19 (d, p-cymene), 3.72 (q), 3.62 (t, 2H), 2.96 (t, 2H), 2.91 (sept, 1H), 2.51 (tt, 3H), 2.20 (s, 3H), 2.10 (m, 2H), 1.25 (d, 3H) and 1.19 (d, 3H) ppm. ¹³C-NMR (CDCl₃, 75 MHz); 291.8 and 135.9 ppm.

EXAMPLE 47 – ring opening metathesis polymerisation of norbornene monomers

Ring opening metathesis polymerisation of various norbornene monomers was performed during 4 hours at 80 °C in toluene (1 ml) as a solvent, while using the Schiff base ruthenium complexes of example 46 as catalysts in a molar ratio norbornene monomer/catalyst equal to 800. The following table 17 indicates the polymerisation yield for each complex and, when the heterogeneous catalyst [91] was used, the properties (number average molecular weight, polydispersity) of the polymer formed.

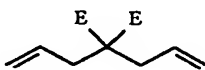
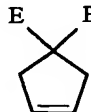


Table 17

Substrate	yield [%]		Polymer properties catalyst 91	
	91	92	$M_n (\times 10^{-3})$ [g/mol]	M_w/M_n
				
R = H	100	100	101.8	1.80
R = ethyl	94	100	135.1	1.86
R = butyl	96	73	162.5	1.87
R = hexyl	82	78	169.5	1.79
R = decyl	56	81	150.0	1.76
R = ethylidene	92	90	112.0	1.84
R = phenyl	68	53	171.5	1.89
R = cyclohexenyl	77	87	149.1	1.80
R = chloromethyl	75	77	107.0	1.70
R = triethoxysilyl	86	90	241.7	1.79
	80	92	22.3	1.70

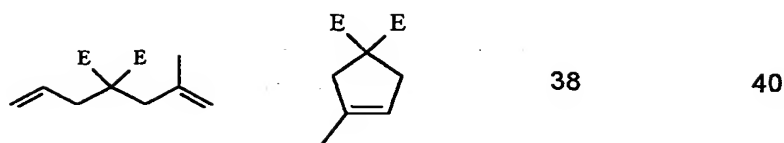
EXAMPLE 48 – ring closing metathesis of α,ω -diolefins

- 5 Ring closing metathesis of the α,ω -diolefins shown in table 18 (wherein E = CO₂C₂H₅) was performed during 4 hours at 70 °C in deuterated benzene as a solvent, while using the Schiff base ruthenium complexes of example 46 as catalysts in a molar ratio diolefin/catalyst equal to 20. Table 18 indicates the conversion obtained with each complex.

Table 18

Substrate	End product	conversion [%]	
		91	92
		89	100
		90	100

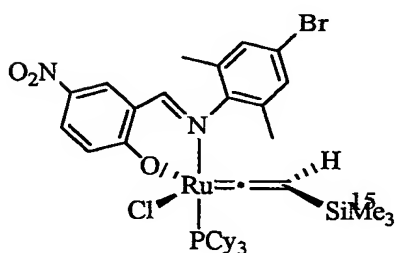
77



EXAMPLE 49 – preparation of ruthenium metal complexes wherein the carbene ligand contains a terminal silyl moiety

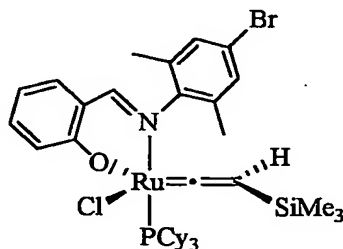
Ruthenium metal complexes wherein the carbene ligand contains a terminal silyl moiety were prepared according to the foregoing procedures, but starting from an alkyne having such a terminal silyl moiety. In this way we prepared :

- chloro-tricyclohexylphosphino-N,O[N-(4-bromo-2,6-dimethylphenyl)-(4-nitro-1-phenyl)iminomethane]-trimethylsilylvinylidene ruthenium [123] which was further characterised by proton and phosphorus nuclear magnetic resonance as follows:



^1H NMR (C_6D_6 , 25 °C): 8.24 (d, 1H), 8.10-7.11 (m, H), 3.61 (t), 2.51 (s, 3H), 1.78-1.30 (m, 20H), 1.54 (s, 6H) and 0.32 (s, 9H) ppm; ^{31}P NMR (122, C_6D_6): 47.07 (s) ppm.

- chloro-tricyclohexylphosphino-N,O[N-(4-bromo-2,6-dimethylphenyl)-(1-phenylimino-methane)-trimethylsilylvinylidene ruthenium [122] which was further characterised by proton and phosphorus nuclear magnetic resonance as follows: ^1H NMR (C_6D_6 , 25°C): 7.53 (d, 1H), 7.24-7.055 (m, 6H), 3.57 (t), 2.48 (s, 3H), 1.72-1.27 (m, 20H), 1.27 (s, 6H), 1.19 (m, 10H) and 0.305 (s, 9H) ppm; ^{31}P NMR (122, C_6D_6): 43.51 (s) ppm.



EXAMPLE 50 – ring opening metathesis polymerisation of strained cyclic monomers

Ring opening metathesis polymerisation of R-substituted norbornene monomers (wherein R has the meaning indicated in table 19), or cyclooctene, was performed at 80 °C in toluene as a solvent, while using the Schiff base ruthenium complex of example 49 as a catalyst in a molar ratio monomer/catalyst equal to 800 (except for cyclooctene: molar ratio 250). The following table 19 indicates the polymerisation yield for each complex and the properties (number average molecular weight, polydispersity) of the polymer formed.

Table 19






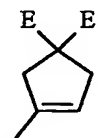
Substrate	time [h]	123		
		yield [%]	M _n	
			($\times 10^4$) [g/mol]	M _w /M _n
R = H	4	100	65.6	1.68
R = ethyl	4	100	60.0	2.43
R = butyl	4	100	107.0	2.20
R = hexyl	4	100	74.3	1.89
R = decyl	4	100	130.4	1.96
R = ethylidene	10	100	94.1	1.91
R = phenyl	4	98	63.5	1.99
R = cyclohexenyl	4	97	96.8	1.97
R = hydroxymethyl	4	65	30.8	1.86
R = chloromethyl	4	100	50.1	2.04
R = triethoxysilyl	4	100	131.1	2.12
cyclooctene	15	100	28.9	1.76

EXAMPLE 51 – ring closing metathesis of α,ω -diolefins

5 Ring closing metathesis of the α,ω -diolefins shown in table 20 (wherein E = CO₂C₂H₅) was performed during 24 hours at 80 °C in deuterated benzene as a solvent, while using the Schiff base ruthenium complexes of example 49 as catalysts in a molar ratio diolefin/catalyst equal to 20. Table 20 indicates the end product yield obtained with each complex.

Table 20

10

Substrate	End product	yield [%]	
		122	123
		100	100
		100	100
		59	69

CLAIMS

1. An at least tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:
- 5 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
 - 10 - a non-anionic unsaturated ligand L¹ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
 - 15 - a non-anionic ligand L² selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
 - 20
2. An at least tetra-coordinated metal complex according to claim 1, wherein the non-anionic ligand L² has constraint steric hindrance.
- 25 3. An at least tetra-coordinated metal complex according to claim 1, wherein the non-anionic ligand L² is selected from the group consisting of methyl, tert-butyl, neopentyl, phenyl and mono- or polysubstituted phenyl such as pentafluorophenyl.
- 30 4. An hexa-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:
- 30 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^m selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
 - 35 - at least one non-anionic bidentate ligand L³ being different from the multidentate ligand; and
 - at most two anionic ligands L⁴, wherein one or more of said anionic ligands L⁴ may be each replaced with a solvent S, in which case the said hexa-coordinated metal complex is a cationic species associated with an anion A.
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5. An hexa-coordinated metal complex according to claim 4, being a bimetallic complex wherein each metal is hexa-coordinated.
6. An hexa-coordinated metal complex according to claim 4 or claim 5, wherein the two metals are the same.
7. An hexa-coordinated metal complex according to claim 4 or claim 5, wherein the two metals are different.
8. An hexa-coordinated metal complex according to any of claims 4 to 7, wherein the at least non-anionic bidentate ligand L^3 is a polyunsaturated C_{3-10} cycloalkenyl or heteroaryl group.
9. An at least tetra-coordinated metal complex according to any of claims 1 to 3 or hexa-coordinated metal complex according to any of claims 4 to 8, wherein the multidentate ligand is a bidentate or tridentate Schiff base.
10. An at least tetra-coordinated metal complex or hexa-coordinated metal complex according to claim 9, wherein the multidentate ligand is a bidentate Schiff base having one of the general formulae (IA) or (IB) referred to in figure 1, wherein:
 - Z is selected from the group consisting of oxygen, sulphur, selenium, $NR^{''''}$, $PR^{''''}$, $AsR^{''''}$ and $SbR^{''''}$, wherein $R^{''''}$ is a radical selected from the group consisting of hydrogen, C_{1-7} alkyl, C_{3-10} cycloalkyl, aryl and heteroaryl;
 - $R^{''}$ and $R^{'''}$ are each a radical independently selected from the group consisting of hydrogen, C_{1-6} alkyl, C_{3-8} cycloalkyl, aryl and heteroaryl, or $R^{''}$ and $R^{'''}$ together form an aryl or heteroaryl radical, each said radical being optionally substituted with one or more, preferably 1 to 3, substituents R_5 each independently selected from the group consisting of halogen atoms, C_{1-7} alkyl, C_{1-7} alkoxy, aryl, alkylsulfonate, arylsulfonate, alkylphosphonate, arylphosphonate, alkylammonium and arylammonium; and
 - R' is either as defined for $R^{''}$ and $R^{'''}$ when included in a Schiff base having the general formula (IA) or, when included in a Schiff base having the general formula (IB), is selected from the group consisting of C_{1-7} alkylene and C_{3-10} cycloalkylene, the said alkylene and cycloalkylene group being optionally substituted with one or more substituents R_5 .
11. An at least tetra-coordinated metal complex or hexa-coordinated metal complex according to any of claims 1 to 10, wherein the metal is a transition metal selected from the group consisting of groups 4, 5, 6, 7, 8, 9, 10, 11 and 12 of the Periodic Table.
12. An at least tetra-coordinated metal complex or hexa-coordinated metal complex according to any of claims 1 to 11, wherein the metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum,

copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

13. A tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- 5 - two anionic ligands L⁸;
- a non-anionic unsaturated ligand L⁹ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₇ alkyl groups or with electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- 10 - a ligand L¹⁰ being a saturated aliphatic monoamine selected from primary amines, secondary amines, cyclic secondary amines and tertiary amines, or a secondary or tertiary diamine,

15 wherein the metal is selected from the group consisting of iridium, ruthenium, osmium, iron, molybdenum, tungsten, titanium, rhenium, technetium, lanthanum, copper, chromium, manganese, palladium, platinum, rhodium, vanadium, zinc, cadmium, mercury, gold, silver, nickel and cobalt.

20 14. A catalytic system comprising:

(a) as the main catalytic species, an hexa-coordinated metal complex according to any of claims 4 to 7, or a tetra-coordinated metal complex according to claim 13, or an at least tetra-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:

- 25 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^{'''} selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- a non-anionic unsaturated ligand L⁵ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₆ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- 30 - a ligand L⁶ being either an anionic ligand or a non-anionic ligand selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
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(b) one or more second catalyst components being selected from the group consisting of Lewis acid co-catalysts (b_1), catalyst activators (b_2) and initiators having a radically transferable atom or group (b_3).

- 5 15. A metal complex according to any of claims 4 to 8 or claim 13, or a catalytic system according to claim 14, wherein each anionic ligand L^4 , L^6 or L^8 is independently selected from the group consisting of C_{1-20} carboxylate, C_{1-20} alkoxy, C_{2-20} alkenyloxy, C_{2-20} alkynyloxy, aryloxy, C_{1-20} alkoxycarbonyl, C_{1-7} alkylthio, C_{1-20} alkylsulfonyl, C_{1-20} alkylsulfinyl, C_{1-20} alkylsulfonate, arylsulfonate, C_{1-20} alkylphosphonate, arylphosphonate, C_{1-20} alkylammonium, arylammonium,

10 alkylidicketonate, arylidicketonate, halogen, nitro and cyano.
16. A catalytic system according to claim 14 or claim 15, wherein the second catalyst component includes a co-catalyst (b_1) selected from the group consisting of boron trihalides; trialkylboron; triarylboron; organoaluminum compounds; magnesium halides; aluminum halides; titanium or

15 vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.
17. A catalytic system according to any of claims 14 to 16, wherein the second catalyst component includes, as a co-catalyst (b_1), an organoaluminum compound selected from the group consisting of tri-n-alkylaluminums; dialkylaluminum hydrides, trialkenylaluminums,

20 alkylaluminum alkoxides, dialkylaluminum alkoxides, dialkylaluminum aryloxides and dialkylaluminum halides.
18. A catalytic system according to claim 14 or claim 15, wherein the second catalyst component includes, as a catalyst activator (b_2), a diazo compound.
- 25 19. A catalytic system according to claim 14 or claim 15, wherein the second catalyst component includes, as an initiator having a radically transferable atom or group (b_3), a compound having the formula $R_{35}R_{36}R_{37}CX_1$, wherein:
 - X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-7} alkyl groups and phenyl-substituted C_{1-7} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered

30 heterocyclic ring (in accordance with the definition of heteroaryl above), and
 - R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting

35 of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene

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group of 2 to 5 carbon atoms), COCl, OH, CN, C₂₋₂₀ alkenyl (preferably vinyl), C₂₋₂₀ alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C₂₋₂₀ alkenyl.

20. A supported catalyst for use in a heterogeneous catalytic reaction, comprising:

- 5 (a) a catalytically active at least tetra-coordinated metal complex or hexa-coordinated metal complex according to any of claims 1 to 12 or a tetra-coordinated metal complex according to claim 13, or a catalytic system according to any of claims 14 to 19, and
- 10 (b) a supporting amount of a carrier suitable for supporting said catalytically active metal complex or catalytic system (a).

21. A method of performing an olefin or acetylene metathesis reaction or a reaction involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises a metal complex selected from the group consisting of hexa-coordinated metal complexes according to any of claims 4 to 7 or tetra-coordinated metal complexes according to claim 13, or at least tetra-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- 20 - a multidentate ligand being coordinated with the metal by means of a nitrogen atom and at least one heteroatom selected from the group consisting of oxygen, sulphur, selenium, nitrogen, phosphorus, arsenic and antimony, wherein each of nitrogen, phosphorus, arsenic and antimony is substituted with a radical R^{'''} selected from the group consisting of hydrogen, C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl;
- 25 - a non-anionic unsaturated ligand L⁵ selected from the group consisting of aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, the said aromatic or unsaturated cycloaliphatic group being optionally substituted with one or more C₁₋₆ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide; and
- 30 - a ligand L⁶ being either an anionic ligand or a non-anionic ligand selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic, the said group being optionally substituted with one or more preferably electron-withdrawing substituents such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide,
- 35

or five-coordinate metal complexes, salts, solvates or enantiomers thereof, comprising a carbene ligand, a multidentate ligand and one or more other ligands, wherein at least one of said other ligands is a constraint steric hindrance ligand having a pK_a of at least 15,

or tetra-coordinated or penta-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- a tetradentate ligand comprising two Schiff bases, and
- optionally a solvent ligand, the said metal complex then being associated with an anion, or tetra-coordinated or penta-coordinated metal complexes, salts, solvates or enantiomers thereof, comprising:

- 5 - at least one bidentate phosphine ligand, and
 - at least one other ligand being selected from solvent ligands, in which case the complex is a cationic species associated with an anion, anionic ligands and non-anionic ligands.

22. A method according to claim 21, wherein said reaction involving the transfer of an atom or group to an olefin or another reactive substrate is selected from the group consisting of:

- 10 - atom or group transfer radical polymerisation of one or more radically (co)polymerisable monomers, especially mono- and diethylenically unsaturated monomers;
 - atom transfer radical addition of a polyhalomethane having the formula CX_nH_{4-n} , wherein X is halogen and n is an integer from 2 to 4, onto an ethylenically unsaturated compound to
15 produce the corresponding saturated polyhalogenated adduct;
 - vinylation reaction of a mono- or di-alkyne with a mono- or di-carboxylic acid to produce alk-1-enyl esters or enol esters or Markovnikov adducts or anti- Markovnikov adducts or mixtures thereof;
 - cyclopropanation of an α -ethylenically unsaturated compound for producing an organic
20 compound having one or more cyclopropane structural units;
 - quinoline synthesis through oxidative cyclisation of 2-aminobenzyl alcohol with ketones;
 - epoxidation of α -ethylenically unsaturated compounds for producing epoxides;
 - oxidation of organic compounds including the oxidation of saturated hydrocarbons for
25 producing alcohols, or sulfides for producing sulfoxides and sulfones, or phosphines for producing phosphonates, or alcohols and aldehydes for producing carboxylic acids;
 - cyclopropenation of an alkyne for producing an organic compound having one or more cyclopropene structural units;
 - hydrocyanation of α -ethylenically unsaturated compounds for producing saturated nitriles, or alkynes for producing unsaturated nitriles, or α,β -unsaturated aldehydes or ketones for
30 producing β -cyano carbonyl compounds;
 - hydrosilylation of olefins for producing saturated silanes, or alkynes for producing unsaturated silanes, or ketones for producing silyl ethers, or trimethylsilylcyanation of aldehydes for producing cyanohydrin trimethylsilyl ethers;
 - aziridination of imines or alkenes for producing organic compounds having one or more
35 aziridine structural units;
 - hydroamidation of olefins for producing saturated amides;
 - hydrogenation of olefins for producing alkanes, or ketones for producing alcohols;
 - aminolysis and hydroamination of olefins for producing saturated primary or secondary amines, and hydroamination of alkynes for producing unsaturated amines;
40 - isomerisation of alcohols, preferably allylic alcohols, for producing aldehydes;

- Grignard cross-coupling of alkyl or aryl halides for producing alkanes or arylalkanes;
 - hydroboration of olefins for producing alkylboranes and trialkylboranes;
 - hydride reduction of aldehydes and ketones for producing alcohols;
 - 5 - aldol condensation of saturated carboxyl compounds for producing α,β -unsaturated carboxyl compounds or β -hydroxycarbonyl compounds, and intra-molecular aldol condensation of dialdehydes or diones for producing cyclic α,β -unsaturated carboxyl compounds;
 - Michael addition of a ketone or a β -dicarbonyl compound onto an α,β -unsaturated carboxyl compound for producing saturated polycarboxyl compounds;
 - 10 - Robinson annulation for producing saturated polycyclic carboxyl compounds;
 - Heck reactions of an aryl halide or a 1-hetero-2,4-cyclopentadiene or a benzo-fused derivative thereof with an α -ethylenically unsaturated compound for producing arylalkenes or heteroarylalkenes;
 - codimerisation of alkenes for producing higher saturated hydrocarbons or alkynes for producing higher alkenes;
 - 15 - hydroxylation of olefins for producing alcohols;
 - alkylation, preferably allylic alkylation, of ketones for producing alkylated ketones, preferably allylic ketones;
 - Diels-Alder reactions such as the cycloaddition of a conjugated diene onto an α -ethylenically unsaturated compound for producing optionally substituted cyclohexenes, or the cycloaddition of furan onto an α -ethylenically unsaturated compound for producing optionally substituted 7-oxanorbornenes;
 - 20 - Suzuki-Miyaura cross-coupling reactions;
 - silylmatalation of unsaturated compounds, particularly olefins and carbonyl compounds;
 - 25 and
 - carbometalation reactions of silyl cyanides and allyl silanes with carbonyl compounds and olefins.
23. A method according to claim 21 or claim 22, wherein the multidentate ligand of the said at least
- 30 tetra-coordinated metal complex is a bidentate or tridentate Schiff base.
24. A method according to claim 21, wherein the said metathesis reaction is the ring-opening metathesis polymerisation of strained cyclic olefins.
- 35 25. A method according to claim 21, wherein the said reaction is the ring-opening metathesis polymerisation of cyclic olefins and is performed in the presence of a Lewis acid co-catalyst (b_1) and/or a catalyst activator (b_2).
26. A method according to claim 25, wherein the Lewis acid co-catalyst (b_1) is selected from the
- 40 group consisting of boron trihalides; trialkylboron; triarylboron; organoaluminum compounds;

magnesium halides; aluminum halides; titanium or vanadium trihalides or tetrahalides or tetraalkoxides; antimony and bismuth pentahalides.

27. A method according to claim 25 or claim 26, wherein the co-catalyst (b₁) is an organoaluminum compound selected from the group consisting of tri-n-alkylaluminums; dialkylaluminum hydrides, trialkenylaluminums, alkylaluminum alkoxides, dialkylaluminum alkoxides, dialkylaluminum aryloxides and dialkylaluminum halides.
28. A method according to claim 25, wherein the catalyst activator (b₂) is a diazo compound.
29. A method according to any of claims 21 to 28, wherein the catalytic component is supported on a carrier.
30. A method according to claim 29, wherein the said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.
31. An at least penta-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:
- a tetradentate ligand comprising two Schiff bases, wherein the nitrogen atoms of said two Schiff bases are linked with each other through a C₁₋₇ alkylene or arylene linking group A; and
 - one or more non-anionic ligands L⁷ selected from the group consisting of (i) trisubstituted phosphines PR₃ wherein R is a radical selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl and heteroaryl; and (ii) aromatic and unsaturated cycloaliphatic groups, preferably aryl, heteroaryl and C₄₋₂₀ cycloalkenyl groups, wherein the said aromatic or unsaturated cycloaliphatic group is optionally substituted with one or more C₁₋₇ alkyl groups or electron-withdrawing groups such as, but not limited to, halogen, nitro, cyano, (thio)carboxylic acid, (thio)carboxylic acid (thio)ester, (thio)carboxylic acid (thio)amide, (thio)carboxylic acid anhydride and (thio) carboxylic acid halide.
32. An at least penta-coordinated metal complex according to claim 31, wherein the said non-anionic ligand L⁷ is cymene.
33. An at least penta-coordinated metal complex according to claim 32, wherein the C₁₋₇ alkylene or arylene linking group A is substituted with one or more substituents selected from the group consisting of chloro, bromo, trifluoromethyl and nitro

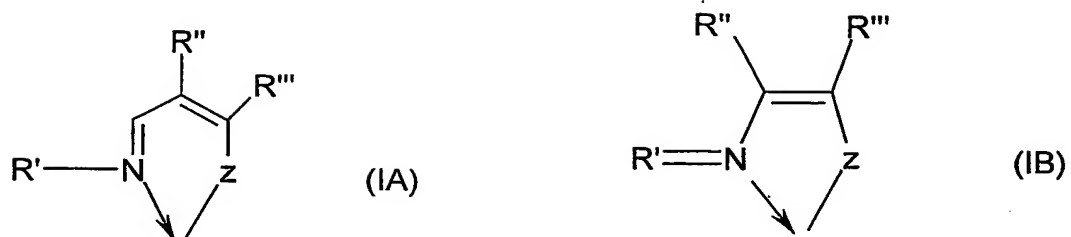
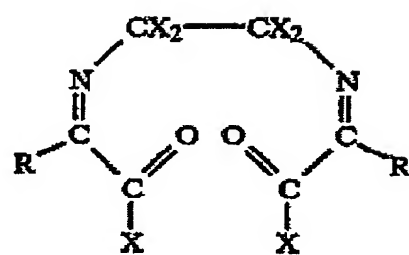
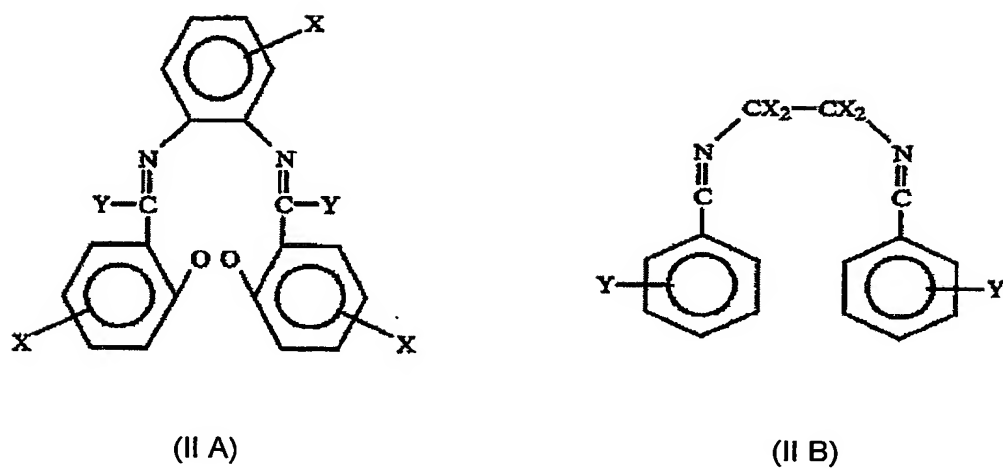
34. An at least penta-coordinated metal complex according to claim 32, wherein each Schiff base of the tetradentate ligand is derived from salicylaldehyde or acetylacetone.
35. An at least penta-coordinated metal complex according to claim 34, wherein the salicylidene or acetylidene group included in each Schiff base is substituted with one or more substituents selected from the group consisting of chloro, bromo, trifluoromethyl and nitro.
36. An at least penta-coordinated metal complex according to any of claims 31 to 35, wherein the tetradentate ligand is selected from the group consisting of *N,N'*-bis(5-nitro-salicylidene)-ethylenediamine, *N,N'*-1,2-cyclohexylenebis(2-hydroxyacetophenonylideneimine), 1,2-diphenylethylenebis(2-hydroxyacetophenonylideneimine) and 1,1'-binaphtalene-2,2'-diamino-bis(2-hydroxyacetophenonylideneimine).
37. A catalytic system comprising:
- as the main catalytic species, an at least penta-coordinated metal complex according to any of claims 31 to 36, and
 - one or more co-catalysts or initiators for the main catalytic species.
38. A catalytic system according to claim 37, wherein the co-catalyst or initiator is selected from amines, preferably secondary amines; organoaluminum compounds; and initiators having a radically transferable atom or group.
39. A catalytic system according to claim 37 or claim 38, wherein the initiator having a radically transferable atom or group is selected from the group of initiators having the formula $R_{35}R_{36}R_{37}CX_1$ wherein:
- X_1 is selected from the group consisting of halogen, OR_{38} (wherein R_{38} is selected from C_{1-20} alkyl, polyhalo C_{1-20} alkyl, C_{2-20} alkynyl (preferably acetylenyl), C_{2-20} alkenyl (preferably vinyl), phenyl optionally substituted with 1 to 5 halogen atoms or C_{1-6} alkyl groups and phenyl-substituted C_{1-6} alkyl), SR_{39} , $OC(=O)R_{39}$, $OP(=O)R_{39}$, $OP(=O)(OR_{39})_2$, $OP(=O)OR_{39}$, $O-N(R_{39})_2$ and $S-C(=S)N(R_{39})_2$, wherein R_{39} is aryl or C_{1-20} alkyl, or where an $N(R_{39})_2$ group is present, the two R_{39} groups may be joined to form a 5-, 6- or 7-membered heterocyclic ring (in accordance with the definition of heteroaryl above), and
 - R_{35} , R_{36} and R_{37} are each independently selected from the group consisting of hydrogen, halogen, C_{1-20} alkyl (preferably C_{1-6} alkyl), C_{3-8} cycloalkyl, $C(=O)R_{40}$, (wherein R_{40} is selected from the group consisting of C_{1-20} alkyl, C_{1-20} alkoxy, aryloxy or heteroaryloxy), $C(=O)NR_{41}R_{42}$ (wherein R_{41} and R_{42} are independently selected from the group consisting of hydrogen and C_{1-20} alkyl or R_{41} and R_{42} may be joined together to form an alkylene group of 2 to 5 carbon atoms), $COCl$, OH , CN , C_{2-20} alkenyl (preferably vinyl), C_{2-20} alkynyl, oxiranyl, glycidyl, aryl, heteroaryl, arylalkyl and aryl-substituted C_{2-20} alkenyl.

40. A supported catalyst for use in a heterogeneous catalytic reaction, comprising:
- (a) a catalytically active at least penta-coordinated metal complex according to any of claims 31 to 36 or a catalytic system according to any of claims 37 to 39, and
 - (b) a supporting amount of a carrier suitable for supporting said catalytically active metal complex or catalytic system (a).
41. A supported catalyst according to claim 20 or claim 40, wherein said carrier is selected from the group consisting of porous inorganic solids, such as amorphous or paracrystalline materials, crystalline molecular sieves and modified layered materials including one or more inorganic oxides, and organic polymer resins.
42. A method of performing a reaction involving the transfer of an atom or group to an ethylenically or acetylenically unsaturated compound or another reactive substrate in the presence of a catalytic component, wherein the said catalytic component comprises an at least penta-coordinated metal complex according to any of claims 31 to 36.
43. A method according to claim 42, wherein the said reaction is an atom transfer radical polymerisation and wherein the said catalytic component is combined with an initiator having a radically transferable atom or group.
44. A method according to claim 42, wherein the said reaction is the cyclopropanation of α -ethylenically unsaturated compounds and wherein the said reaction is effected in the presence of a diazo compound.
45. An at least tetra-coordinated metal complex or hexa-coordinated metal complex according to claim 9, wherein the multidentate ligand is a bidentate Schiff base being selected from the group consisting of:
- reaction products of an optionally substituted salicylaldehyde or a nitration product thereof with a primary amine, as shown in formula (VI) of figure 6, wherein A is selected from the group consisting of oxygen, sulfur and nitrogen; R is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl, provided that R represents at least one hydrogen atom and z is 1 when A is oxygen or sulfur or z is 2 when A is nitrogen; R¹ is selected from the group consisting of C₁₋₇ alkyl, aryl, arylalkyl, siloxyl, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl; R² is selected from the group consisting of hydrogen, C₁₋₇ alkyl, aryl and halogen; R³ is hydrogen; R⁴ is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl; and R⁵ is selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl, aryl, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl; and
 - reaction products of an optionally substituted pyrrole-2-carboxaldehyde with a primary amine as shown in formula (V) of figure 6, wherein R¹ is selected from the group consisting

of C₁₋₇ alkyl, aryl, arylalkyl, siloxyl, nitro, sulfonate, halogen, alkyloxyalkyl, aryloxyalkyl, aryloxyaryl and alkyloxyaryl; R² is selected from the group consisting of hydrogen, C₁₋₇ alkyl, aryl and halogen; R³ is hydrogen; R⁴ is selected from the group consisting of hydrogen, C₁₋₇ alkyl and aryl; and R⁵ is selected from the group consisting of C₁₋₇ alkyl, C₃₋₁₀ cycloalkyl and aryl.

46. An at least tetra-coordinated metal complex or hexa-coordinated metal complex according to claim 45, wherein said primary amine is an arylamine having one or more bulky substituents such as 2,6-diisopropylaniline, 2,6-diisopropyl-4-nitroaniline, biphenylamine, terphenylamine, anthracenylamine, phenanthracenylamine, 2,6-dimethylphenyl, 2,6-diethylaniline, 4-methylaniline, 2-isopropyl-6-methylaniline, 2,4,6-trimethylaniline, 2-*tert*-butylaniline, 2-*tert*-butyl-6-methylaniline and 10-nitroanthracenylamine.
47. A penta-coordinated metal complex, a salt, a solvate or an enantiomer thereof, comprising:
- a bidentate Schiff base ligand,
 - an anionic ligand,
 - a non-anionic ligand, and
 - a Fischer carbene ligand.
49. A penta-coordinated metal complex according to claim 47, being selected from the group consisting of:
- chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium,
 - chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy-5-nitro)-1-phenyl)iminomethane]-ruthenium,
 - chloro-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium,
 - toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate,
 - toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(4-bromo-2,6-dimethylphenyl)-((2-phenoxy-5-nitro)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate, and
 - toluyl-tricyclohexylphosphino-ethoxyvinylidene-N,O[N-(2,6-diisopropylphenyl)-((2-phenoxy)-1-phenyl)iminomethane]-ruthenium tetrafluoroborate.

1 / 4

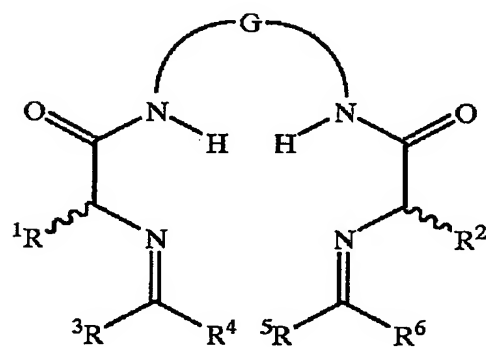
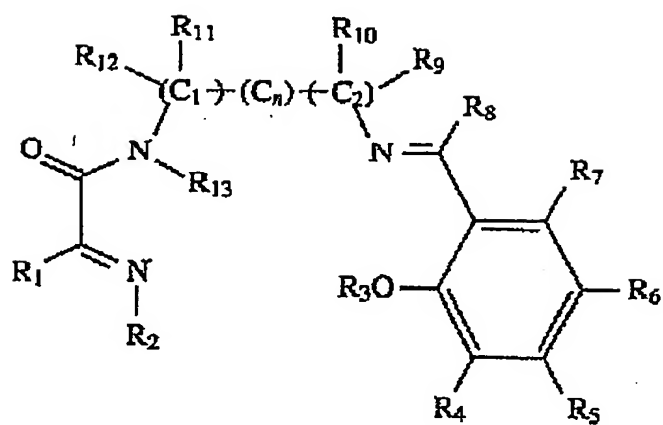
Figure 1Figure 2

(II C)

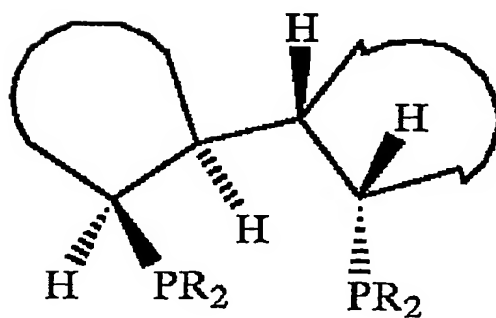
2 / 4

Figure 3

(IIIA)



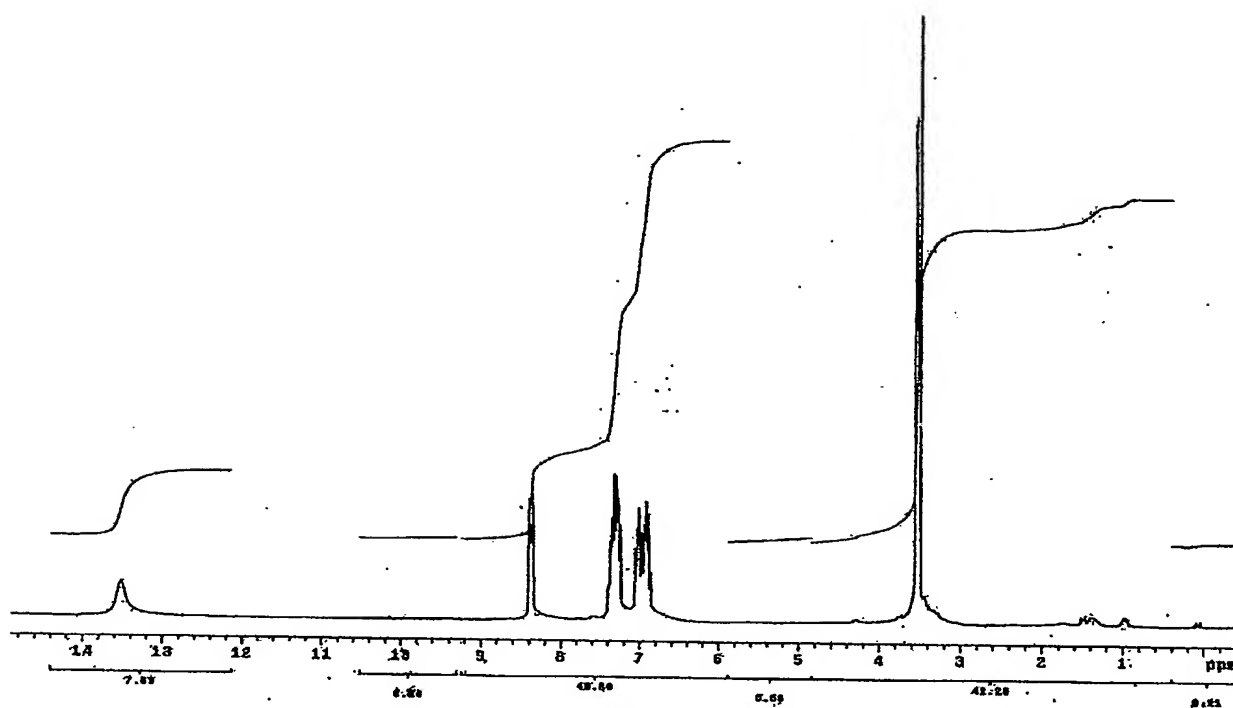
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(IIIC)

3 / 4

Figure 4



4 / 4

Figure 5

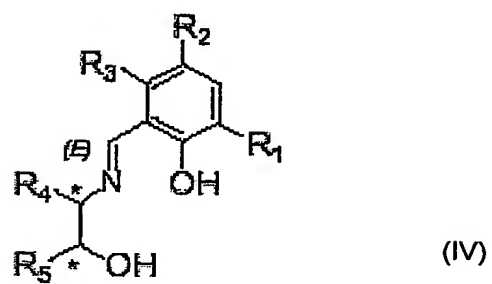
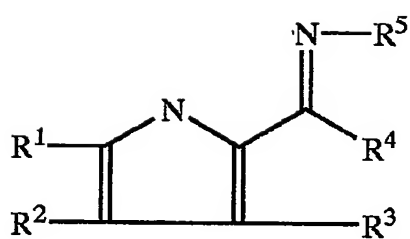
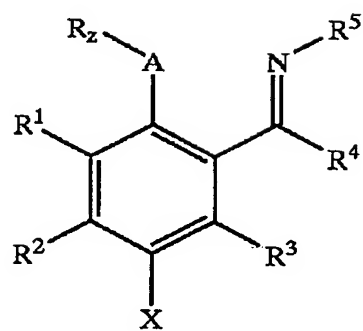


Figure 6



(V)



(VI)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
21 April 2005 (21.04.2005)

PCT

(10) International Publication Number
WO 2005/035121 A3

(51) International Patent Classification⁷: **B01J 31/22**,
31/02, C07C 6/04

(21) International Application Number:
PCT/BE2004/000146

(22) International Filing Date: 15 October 2004 (15.10.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
03447257.1 16 October 2003 (16.10.2003) EP
60/529,010 12 December 2003 (12.12.2003) US

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(81) Designated States (unless otherwise indicated, for every
kind of national protection available): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,
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MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,
ZW.

(84) Designated States (unless otherwise indicated, for every
kind of regional protection available): ARIPO (BW, GH,
GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM,
ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
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GW, ML, MR, NE, SN, TD, TG).

Declaration under Rule 4.17:

— of inventorship (Rule 4.17(iv)) for US only

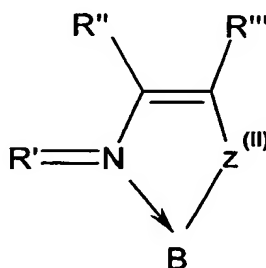
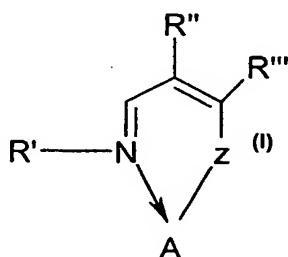
Published:

— with international search report
— before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

(88) Date of publication of the international search report:
30 June 2005

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: SCHIFF BASE METAL COMPLEXES FOR USE AS CATALYSTS IN ORGANIC SYNTHESIS



(57) Abstract: This invention relates to metal complexes which
are useful as catalysts components in olefin metathesis reactions,
atom or group transfer radical polymerisation or addition reac-
tions and vinylation reactions.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE2004/000146

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/22 B01J31/02 C07C6/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>VERPOORT ET AL: "Easily accessible ring opening metathesis and atom transfer radical polymerization catalysts based on arene, norbornadiene and cyclooctadiene ruthenium complexes bearing Schiff base ligands"</p> <p>ADVANCED SYNTHESIS AND CATALYSIS, vol. 345, no. 3, March 2003 (2003-03), pages 393-401, XP002317376</p> <p>page 395, column 1, paragraph 1; tables 2,3; compound 6</p> <p style="text-align: center;">----- -/--</p>	<p>1-3, 9-12,14, 16-18, 20-28, 45,46</p>

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

11 February 2005

Date of mailing of the international search report

24.05.05

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Klaes, D

INTERNATIONAL SEARCH REPORT

International Application No
PCT/BE2004/000146

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	BRUNNER ETAL: "Synthesis, properties, stereochemistry and crystal structures of diastereomeric benzene-ruthenium(II) complexes with a chiral salicylideneaminato ligand" J. CHEM. SOC., DALTON TRANSACTIONS, 1996, pages 1499-1508, XP002317377 compound 4A -----	1,2, 9-11,45
X	BRUNNER ET AL: "Stereochemistry and the chiral ruthenium atom in half-sandwich compounds.X-ray Structure analysis and appeal for the proper use of stereochemical terminology" INORG. CHEM., vol. 34, 1995, pages 3349-3351, XP002317378 Scheme 1 -----	1,2, 9-12,45
A	VERPOORT ET AL: "Ring-closing metathesis, Kharasch addition and enol ester synthesis by a novel class of ruthenium (II) complexes" TETRAHEDRON LETTERS, vol. 42, 2001, pages 8959-8963, XP002317379 the whole document -----	1-3, 9-12,14, 16-30, 41,45,46
A	VERPOORT ET AL: "A new class of ruthenium complexes containing Schiff base ligands as promising catalysts for atom transfer radical polymerisation and ring opening metathesis polymerization" JOURNAL OF MOLECULAR CATALYSIS A, vol. 180, 2002, pages 67-76, XP002317380 the whole document -----	1-3, 9-12,14, 16-30, 41,45,46
A	WO 03/062253 A (UNIVERSITEIT GENT; VERPOORT, FRANCIS, WALTER, CORNELIUS; DE CLERCQ, BO) 31 July 2003 (2003-07-31) the whole document -----	1-3, 9-12,14, 16-30, 41,45,46

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BE2004/000146

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3, 9 (part), 10-12 (all part), 14 (part), 16-30 (all part), 41 (part), 45
46

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

The application is not in accordance with Art. 5 and 6 EPC. Independent process claim 1 claims a very broad range of complexes. But examples are only given for specific complexes. The multidentate ligands which are an essential feature of the inventions are exclusively derivatives of the Schiff base salicylaldimine. All specific complexes bear Ru. The examples are limited to ligands L1 = cymene, 1-4-cyclooctadiene and norbornadiene.

It is not disclosed how the broad range of ligands and metals shall be combined in order to obtain efficient catalysts. Therefore it is not clear which features are essential for the inventions.

Therefore, the search for the 1. invention has been limited to ruthenium complexes according to the first invention bearing a) a salicylaldimine derivative, b) an aryl or unsaturated cycloalkene and c) a non-anionic ligand selected from the group consisting of C1-7-Alkyl, C3-10-Cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic; catalytic systems comprising said complex and metathesis reactions in presence of the same.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-3, 9 (part), 10-12 (all part), 14 (part) , 16-30 (all part), 41 (part), 45, 46

Catalyst according to examples 2-8 and 10 comprising a) a multidentate ligand being coordinated with the metals by means of a nitrogen and at least one heteroatom; b) a non-anionic unsaturated ligand selected from aromatic and unsaturated cycloaliphatic compounds and c) a non-anionic ligand selected from the group consisting of C1-7-Alkyl , C3-10-Cycloalkyl, aryl, arylalkyl, alkylaryl and heterocyclic; catalytic systems comprising said catalyst and metathesis reactions in presence of the same

2. claims: 4-8, 9 (part), 10-12 (all part), 14-20 (all part), 21-30 (all part), 41 (part)

Hexacoordinated catalysts according to examples 10 and 11 comprising a) a multidentate ligand being coordinated with the metals by means of a nitrogen and at least one heteroatom; b) at least one non-anionic bidentate ligand being different from a); and c) at most two anionic ligands, catalytic systems comprising said complexes and metathesis reactions in presence of the same.

3. claims: 13, 14-20 (all part), 21-30 (all part), 41 (part)

A tetra-coordinated complex according to example 44 comprising a) two anionic ligands b) a non-anionic unsaturated ligand selected from the group consisting of aromatic and unsaturated cycloaliphatic groups and c) a saturated aliphatic monoamine; catalytic systems comprising the same and metathesis reactions in presence of the same.

4. claims: 31-40, 42-44

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

An at least penta-coordinated metal complex comprising a) a ligand comprising two Schiff bases, wherein the nitrogen atoms are linked with each other through a C1-7 alkylene or arylene group and b) one or more non-anionic ligands selected from the group consisting of i) trisubstituted phosphines, ii) aromatic and unsaturated cycloaliphatic groups catalytic systems comprising the same and atom transferring reactions (like cyclopropanation reactions) in presence of the same.

5. claims: 47, 49

Penta-coordinated metal complexes according to examples 15-17, 46 and 49 comprising a) a bidentate Schiff base ligand, b) an anionic ligand, c) a non-anionic ligand and d) a Fischer carbene ligand.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE2004/000146

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 03062253	A	31-07-2003	EP 1329455 A1	23-07-2003
			WO 03062253 A1	31-07-2003
			CA 2473029 A1	31-07-2003
			EP 1468004 A1	20-10-2004
			US 2005043541 A1	24-02-2005
